

Sheffield Hallam University

Organoclays: Preparation, characterisation and use as sorbents and catalysts.

WATSON, Ruth.

Available from the Sheffield Hallam University Research Archive (SHURA) at:

<http://shura.shu.ac.uk/20504/>

A Sheffield Hallam University thesis

This thesis is protected by copyright which belongs to the author.

The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the author.

When referring to this work, full bibliographic details including the author, title, awarding institution and date of the thesis must be given.

Please visit <http://shura.shu.ac.uk/20504/> and <http://shura.shu.ac.uk/information.html> for further details about copyright and re-use permissions.

CITY CAMPUS PCND STREET
SHEFFIELD S1 1WB

1740

101 546 709 1



372560

Sheffield Hallam University

REFERENCE ONLY

ProQuest Number: 10701151

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 10701151

Published by ProQuest LLC (2017). Copyright of the Dissertation is held by the Author.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code
Microform Edition © ProQuest LLC.

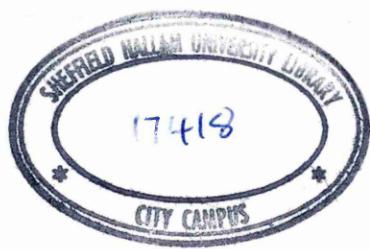
ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

**Organoclays: Preparation, Characterisation and
Use as Sorbents and Catalysts**

Ruth Watson

A thesis submitted in partial fulfilment of the requirements of
Sheffield Hallam University
for the degree of Doctor of Philosophy

August 1997



ABSTRACT

This thesis reports the interactions of (poly)cations with a variety of clay minerals and the application of the resultant organoclays as both sorbents and catalysts. The behaviour of organoclays containing tetramethylammonium cations (TMA^+), is compared to the behaviour of organoclays containing polycations of the formula $[(\text{Me}_2\text{NCH}_2\text{CHOHCH}_2)_n]^{n+}$ (MagnaFloc 206), which are shown to form two distinct types of organoclay.

To investigate the interactions of the (poly)cations with clay surfaces, several dry powder analysis techniques have been employed including Kjeldahl nitrogen analysis, variable temperature x-ray diffraction and thermogravimetric analysis. The studies have shown that the (poly)cations reside between the clay layers and that the nature of the clay and the resident exchange cation have a significant effect on the amount adsorbed. It is also shown that the polycations have a higher affinity than tetramethylammonium cations for all the clay minerals investigated.

Sorbents exchanged with various amounts of (poly)cation are investigated for their ability to adsorb benzene and *p*-nitrophenol from water. The adsorption by polycation containing sorbents is reduced compared to TMA^+ containing sorbents and the latter is comparable with that reported in the literature. The adsorption site in such sorbents is the siloxane surface in the clay interlayers, as shown by the observation that the uptake of both benzene and *p*-nitrophenol by TMA^+ exchanged SAz-1, a high charge montmorillonite, was reduced compared to TMA^+ exchanged SWy-1, a low charge montmorillonite. In SAz-1 there is closer packing of adsorbed TMA^+ cations resulting in less siloxane surface area being available. Hydration of the TMA^+ cations also increases steric constraints. High polycation loadings prevent the clay layers from expanding and thus accessibility of *p*-nitrophenol to the clay surface is reduced. Partition into the organic carbon content of the polymer occurs but uptake does not increase with organic carbon content as expected. Also, TMA^+ exchanged Westone-L was expected to behave similarly to TMA^+ exchanged SWy-1 as Westone-L and SWy-1 have very similar cation exchange capacities. However, it is shown that TMA^+ exchanged Westone-L behaves more like TMA^+ exchanged SAz-1 which has a much higher cation exchange capacity.

A range of organoclays containing either tetraalkylammonium cations or polycations at differing exchange levels have been subjected to acid leaching at either 25 or 90°C. The activity of these acid-activated (poly)cation-exchanged clays for the conversion of α -pinene to camphene and limonene was determined and compared with those from clay samples (without (poly)cations), acid-treated in the same manner. The presence of the polycation had a more marked influence on the activity of samples derived from SAz-1 than for corresponding samples derived from SWy-2, which was attributed to the increased hydrophobicity of the polycation loaded clay. Comparable yields for SWy-2 in the absence and presence of polycation suggest that SWy-2 disperses well in the non-polar α -pinene. Also, octadecyltrimethylammonium and dodecyltrimethylammonium exchanged clays were generally less active than TMA^+ exchanged clays which were comparable to the most active polymer containing catalysts. It has also been shown that the octahedral iron content of the clay affects its catalytic activity.

Finally, a competitive adsorption method of catalyst preparation has been developed which may replace more conventional high temperature techniques.

ACKNOWLEDGEMENTS.

A few 'thank-yous' are necessary:

To my supervisor, Dr. Chris Breen, for his encouragement, support and wise words.

To all of the technicians who helped make life a little easier, particularly Paul and Kevin.

To my friends and colleagues (past and present) - despite their 'Bucket Chemist', and 'Dr. Watson' jokes.

To my family for their continued support and encouragement.

Last, but definately not least, to Christopher - without whose endless help and support I may not have made the distance.

TABLE OF CONTENTS.

CHAPTER 1

<i>INTRODUCTION TO THE THESIS</i>	6
1. ENVIRONMENTAL APPLICATIONS OF ORGANOCLAYS.	7
1.1 ORGANOCLAYS.	9
1.2 POLYCATION EXCHANGED CLAYS AS ADSORBENTS FOR POLLUTANTS.....	10
1.3 POLYCATION EXCHANGED CLAYS AS CATALYSTS.....	13
1.4 AIMS.....	15

CHAPTER 2

<i>INTRODUCTION TO CLAY MINERALS</i>	16
2. INTRODUCTION.....	17
2.1 THE STRUCTURE AND FUNDAMENTAL PROPERTIES OF CLAY MINERALS.....	17
2.1.1 The Fundamental Units of Sheet Silicates.....	18
2.1.1.1 Octahedral Sheets.....	18
2.1.1.2 Tetrahedral Sheets.....	19
2.1.1.3 The Formation of Layer Silicates.....	19
2.1.2 Classification.....	21
2.2 ADDITIONAL PROPERTIES OF CLAY MINERALS.....	23
2.3 CATION EXCHANGE CAPACITY (CEC).	24
2.3.1 Determination of CEC.....	25
2.3.2 Isomorphous Substitution.	25
2.3.3 Broken Bonds.	26
2.3.4 The Hydrogen of Exposed Hydroxyls.....	26
2.3.5 Exchangeable Ions and Soluble Salts.	26
2.4 CATION MIGRATION.....	28
2.5 THE HYDRATION AND SWELLING OF CLAY MINERALS.....	28
2.6 INTERPARTICLE ASSOCIATIONS.....	33
2.6.1 Electrical Phenomena at Interfaces.	33
2.6.2 Interparticle Associations in Clay Suspensions.....	34
2.6.2.1 Controlling Flocculation of Clay Suspensions.	37
2.6.2.1.1 Face Charge Reversal.	37
2.6.2.1.2 Edge Charge Reversal.	38
2.7 ACIDIC PROPERTIES OF CLAYS.	38

CHAPTER 3

REVIEW OF THE INTERACTIONS OF CLAY MINERALS WITH ORGANIC COMPOUNDS.....	40
3. INTRODUCTION.....	41
3.1 MECHANISMS OF THE INTERACTIONS OF CLAY MINERALS WITH ORGANIC COMPOUNDS.....	42
3.1.1 Organophilic Clays.....	43
3.1.2 Adsorptive Organoclays.....	44
3.2 TERMS OF ABBREVIATION.....	44
3.3 ADSORPTION ISOTHERMS.....	44
3.4 ORIGIN AND DEVELOPMENT OF ORGANOCLAY COMPLEXES.....	47
3.4.1 Surface Adsorptive Organoclays.....	47
3.4.2 Organophilic Clays.....	53
3.5 INFLUENCE OF EXCHANGEABLE CATIONS.....	57
3.6 SORPTION OF DIFFERENT CLASSES OF CONTAMINANTS.....	57
3.7 ALKYLDIAMMONIUM CLAYS.....	58
3.8 EXAMPLES OF APPLICATIONS.....	59
3.8.1 Personal Monitoring Devices.....	59
3.8.2 In-Situ Modification of Sites.....	59
3.9 SUMMARY OF GENERAL INTERACTIONS.....	60
3.9.1 Adsorption of Organic Cations.....	61
3.9.2 Adsorption of Pollutants from Solution.....	62
3.9.3 Mechanisms of Interaction.....	63
3.10 CLAY-POLYMER INTERACTIONS.....	67
3.10.1 Introduction.....	67
3.10.2 Organic Polymers.....	69
3.10.3.1 Nonionic Polymers.....	71
3.10.3.2 Influence of Molecular Weight.....	72
3.10.3.3 Influence of Exchangeable Cations and Ionic Strength.....	73
3.10.4 Charged Polymers.....	73
3.10.5 Anionic Polymers.....	74
3.10.5.1 Influence of Exchangeable Cations.....	74
3.10.5.2 Influence of Molecular Weight.....	74
3.10.5.3 Influence of pH and Ionic Strength.....	75
3.10.6 Cationic Polymers.....	76
3.10.6.1 Influence of Exchangeable Cations.....	78
3.10.6.2 Influence of Molecular Weight and Cationicity.....	80
3.10.6.3 Influence of pH and Ionic Strength.....	81
3.11 SUMMARY OF CLAY-POLYMER INTERACTIONS.....	83
3.11.1 Mechanisms of Clay-Polymer Interactions and Flocculation.....	83
3.12 ACID TREATED CLAYS.....	88
3.12.1 Applications.....	88
3.12.2 Activation Treatments.....	89
3.12.3 The Effect of Acid Treatment on the Clay Structure.....	90

3.12.4 Measurement of Structural Changes and Acidity.....	93
3.12.5 Ion Exchanged Catalysts.....	95
3.12.5.1 Metal Cations.....	95
3.12.5.2 Pillars.....	96
3.13 CATALYTIC ACTIVITY.....	98
3.13.1 Acid Catalysis of α -Pinene.....	99
3.13.2 Applications.....	100
3.13.3 The Rearrangement of α -Pinene.....	101
3.13.4 Other Solid Catalysts Used for the Conversion of α -Pinene.....	102
3.14 SUMMARY OF ACID TREATMENT	105

CHAPTER 4

<i>EXPERIMENTAL TECHNIQUES, EQUIPMENT AND SAMPLE PREPARATION.....</i>	<i>106</i>
4. INTRODUCTION.....	107
4.1 CLAY MINERALS INVESTIGATED.....	107
4.1.1 Sedimentation / Purification and Ion Exchange.....	108
4.2 TERMS OF ABBREVIATION.....	110
4.3 ORGANIC ADSORBATES.....	110
4.4 ANALYSIS TECHNIQUES USED TO INVESTIGATE THE INTERACTION BETWEEN THE CATIONIC ORGANIC SPECIES AND CLAY.....	111
4.4.1 X-Ray Fluorescence Analysis.....	111
4.4.2 Kjeldahl Nitrogen Analysis.....	111
4.4.2.1 Sample Preparation.....	111
4.4.2.2 Sample Digestion and Analysis.....	112
4.4.2.3 Reproducibility of Kjeldahl Nitrogen Analysis.....	112
4.4.3 X-Ray Diffraction Analysis.....	113
4.4.4 Thermogravimetric Analysis.....	114
4.4.5 % Carbon Analysis.....	114
4.5 CLAY PREPARATION FOR POLLUTION ADSORPTION STUDIES.....	114
4.5.1 Techniques for Measurement of Pollutant Adsorption.....	115
4.5.1.1 Gas Chromatography.....	115
4.5.1.2 Ultra-Violet Spectrophotometry.....	116
4.5.1.3 Reproducibility of Pollutant Adsorption Determinations.....	117
4.6 CLAY PREPARATION FOR CATALYTIC STUDIES.....	117
4.6.1 Techniques Used to Study the Effects of Acid Treatment.....	124
4.7 THE CATALYTIC REACTION	125
4.7.1 Techniques for Measurement of Catalytic Activity and Product Identification.....	126
4.7.1.1 Gas Chromatography.....	126
4.7.1.2 Reproducibility of the Measurement of Catalytic Activity.....	126
4.7.1.3 Gas Chromatography - Mass Spectrometry.....	126
4.8 SAFETY PRECAUTIONS FOR EXPERIMENTAL PROCEDURES	127

CHAPTER 5

<i>INVESTIGATIONS INTO THE ADSORPTION OF CATIONIC SPECIES BY CLAYS.....</i>	<i>128</i>
<i>5. INTRODUCTION.....</i>	<i>129</i>
<i>5.1 XRF DETERMINATION OF THE ELEMENTAL COMPOSITION OF THE CLAYS INVESTIGATED</i>	<i>129</i>
<i>5.2 ORGANOCLAY ADSORPTION.....</i>	<i>130</i>
<i>5.2.1 Kjeldahl Analysis of the Organoclay Complexes.</i>	<i>130</i>
<i>5.2.2 XRD Analysis of Clays And Organoclay Complexes.....</i>	<i>147</i>
<i>5.2.3 Thermogravimetric Analysis of Organoclay Complexes.</i>	<i>153</i>
<i>5.3 SUMMARY OF THE RESULTS OBTAINED FOR (POLY)CATION ADSORPTION.....</i>	<i>156</i>

CHAPTER 6

<i>INVESTIGATIONS INTO THE ADSORPTION OF POLLUTANTS BY ORGANOCLAYS</i>	<i>159</i>
<i>6. INTRODUCTION.....</i>	<i>160</i>
<i>6.1 BENZENE ADSORPTION ON (POLY)CATION EXCHANGED CLAYS..</i>	<i>162</i>
<i>6.2 ADSORPTION OF p-NITROPHENOL ON (POLY)CATION EXCHANGED CLAYS.....</i>	<i>169</i>
<i>6.3 SUMMARY OF RESULTS FOR POLLUTANT ADSORPTION.....</i>	<i>178</i>

CHAPTER 7

<i>INVESTIGATIONS INTO THE CATALYTIC ACTIVITY OF ORGANOCLAYS..</i>	<i>181</i>
<i>7. INTRODUCTION.....</i>	<i>182</i>
<i>7.1 SAMPLES.....</i>	<i>184</i>
<i>7.2 ANALYSIS.</i>	<i>184</i>
<i>7.2.1 XRD Analysis.</i>	<i>184</i>
<i>7.2.2 % Carbon Values.</i>	<i>190</i>
<i>7.2.3 FTIR Analysis.</i>	<i>193</i>
<i>7.2.4 XRF of Acid-Activated Organoclays.</i>	<i>197</i>
<i>7.3 THE CATALYTIC CONVERSION OF α-PINENE.</i>	<i>199</i>
<i>7.4 SUMMARY OF CATALYSIS INVESTIGATIONS.....</i>	<i>220</i>

CHAPTER 8

<i>CONCLUSIONS AND FURTHER WORK.....</i>	223
<i>8. INTRODUCTION.....</i>	224
<i>8.1 (POLY)CATION INTERACTIONS WITH CLAY MINERALS.</i>	224
<i>8.2 POLLUTANT ADSORPTION.</i>	228
<i>8.3 CATALYSIS.....</i>	231

CHAPTER 9

<i>POSTGRADUATE STUDY, ARTICLES IN PREPARATION AND REFERENCES</i>	235
<i>9.1 POSTGRADUATE STUDY.....</i>	236
<i>9.2 ARTICLES IN PREPARATION.....</i>	236
<i>9.3 REFERENCES.....</i>	237

CHAPTER 1

Introduction to the Thesis.

1. ENVIRONMENTAL APPLICATIONS OF ORGANOCLAYS.

Contamination of soils, groundwater, aquifers and other water sources by hazardous organic pollutants has become a major issue in environmental and water quality management and control all over the world^{1,2,3}. The major groups of contaminants encountered in this context are hydrocarbons, halogenated organic compounds and pesticides⁴. Although some of the contamination is the result of isolated incidents or non-agricultural use of pesticides, much is attributable to applications of pesticides to agricultural land according to Good Agricultural Practise. However, large additions of pesticides are necessary to achieve the high productivity demanded by todays society. Hence, contamination of soils is increasing both as a result of the use of chemicals and also the disposal of industrial and domestic wastes to agricultural land. Wastes are frequently added to soils because of their high nitrogen and phosphorous contents, however these wastes are often highly contaminated with organic pollutants which are thus incorporated into soils⁵.

A further source of contamination arises from the disposal of toxic waste. Methods of disposal for such wastes are many and include placement in drums for burial, pooling for evaporation, stabilisation/solidification, incineration, and the dominant way of handling hazardous chemicals which is storage in lined landfill sites. Organic compounds can however be released from waste landfills and contaminate ground water, soil and air⁶. For example, concentrations of phenols as high as 4 ppm have been found in ground water underneath a landfill site⁷.

Treatment of water supplies to remove pesticides is extremely costly to the consumer

and protection of water resources from contamination is a logical long term option. Developing strategies to achieve such protection demands an understanding of the processes that determine pollutant fate in the environment. The transport of contaminants in the environment is a complex process and among other factors, it involves the sorption of these compounds by soil components such as organic materials and clay minerals.

This suggests that clay minerals, which represent a readily available, low cost resource of potentially high surface area material, could be applied to the problem of environmental remediation. However, they have one main disadvantage; their lack of permanent porosity. A natural clay swells upon hydration, but loses its interlayer area after dehydration. Also, the inorganic exchange ions of natural clays which are usually alkali-metal and alkali-earth-metal ions, such as Na^+ and Ca^{2+} , are strongly hydrated in the presence of water resulting in a hydrophilic environment at the clay surface. As a result natural clays are ineffective sorbents for poorly water-soluble, non-ionic, organic contaminants. However, the surface properties of natural clays may be greatly modified by simple ion-exchange reactions.

In 1949 Jordan *et al.*⁸ first noted that a bentonite exhibiting high swelling properties in water showed an aversion to water and a tendency to swell in various organic liquids after reaction with appropriate organic ammonium salts. In 1955 Barrer and MacLeod⁹ reported that exchange of tetramethylammonium and tetraethylammonium ions opened up the lamellae of the clay, and caused profound changes in the sorption of, and the interaction with, organic molecules. In contrast to the lack of interaction with untreated materials, paraffins and aromatic hydrocarbons were freely adsorbed between the

lamellae of the organic-treated montmorillonites. Organic-cation exchanged clays are now widely referred to as 'organoclays'.

1.1 ORGANOCLAYS.

In the 1950s and 1960s it was shown that the sorption of vapours of nonionic organic liquids to organoclays was substantially greater than sorption to Na^+ or Ca^{2+} exchanged clays¹⁰. It was determined that the intercalated organic cations act as 'props' that hold apart the silicate layers, allowing nonionic organic vapours to be intercalated and sorbed. In the absence of these relatively large organic cations, nonionic organic vapours cannot penetrate the interlamellar space of the expandable clay and sorption is limited to the external surfaces of the clay particles.

When large organic surfactant cations of the form $[(\text{CH}_3)_3-\text{NR}]^+$, or $[(\text{CH}_3)_3-\text{NRR}']^+$, (where R and R' are aromatic or alkyl hydrocarbons, and R is large (C_{12} or greater)), occupy the exchange sites of smectite clays, the surface properties change from hydrophilic to organophilic. Once such organic cations are fixed on the smectite clay surface, an organic phase forms that is derived from the alkyl hydrocarbon chain. This organic phase functions as a partition medium for nonionic organic contaminants and is highly effective in removing such compounds from water¹¹.

The sorptive characteristics of organoclays formed using small organic cations such as tetramethylammonium (TMA^+) as exchange ions are much different. Such small organic cations exist as discrete species on the clay surface and do not form an organic partition

phase. Organoclays formed from both types of organic cation are discussed in detail in Chapter 3.

1.2 POLYCATION EXCHANGED CLAYS AS ADSORBENTS FOR POLLUTANTS.

The work reported in this thesis investigates polycation-treated clays as adsorbents for organic pollutants. A favourable entropy term associated with the desorption of many water molecules per single polymer, makes the adsorption of the polymer a rapid and essentially irreversible process. Competitive adsorption between polycations and large excesses of inorganic ions greatly favours polycation adsorption. This is a particular advantage in the potential commercialisation of the adsorbents since the clay would need no pre-exchange procedures. A further processing advantage exists insofar as the polycation is produced as a highly concentrated aqueous solution (40% by weight of polymer). Thus the potential manufacturer would be able to operate at economic, high solids contents without the problems of foaming associated with surfactant treatments.

To date polycation adsorption has only been studied in relation to flocculation of clays in water treatment plants¹² and their propensity as selective sorbents for organic pollutants has not been considered. In principle these polycations offer considerable opportunities for fine tuning of selective adsorption properties. It is well established, as mentioned above, that treatment with long hydrocarbon chain cationic surfactants can change the nature of the surface and it becomes hydrophobic. The advantage of the polycation is that the regularly spaced cationic groups will ensure a more even distribution of organic carbon over the available surface in contrast to the surfactant molecules which associate

in islands on the clay surface, thus forming a supported organic phase into which the pollutants undergo partition. Controlling the length of the spacer group between the cationic groups on the polymer will effect the amount of surface covered by the polymer, and thus the amount of available hydrophilic surface, and the organic carbon content of the clay. Hence, this work can contribute to the debate concerning the mode of uptake, partition or adsorption, on modified clay surfaces.

This work characterises the adsorption of a polyamine (MagnaFloc 206) on clays with different charge densities and looks at the adsorption of benzene, a notorious pollutant, and *p*-nitrophenol. Both are on the Environmental Protection Agency list of Priority Pollutants¹³. Phenol and substituted phenols are some of the most widely used organic compounds in existence, and they are also degradation products of several pesticides. For example, *p*-nitrophenol may be produced during the hydrolytic cleavage of several organophosphorous pesticides.

The behaviour of the polycation exchanged clays is compared to inorganic cation exchanged clays and also TMA⁺ exchanged clays which allows comparison with the results of previous workers.

The polycation exchanged organoclays may have many industrial applications and could compete in many fields where the more common surfactant treated clays are used today.

Environmental applications include:-

- In liner technology to provide an additional barrier to the escape of chemicals from storage tanks and landfill sites.
- Remediation efforts at contaminated sites might include preparation of organic clays from on-site soil materials.
- Components of waste containment barriers¹⁴ and in chemical waste stabilisation.
- Removing organic contaminants from solution.
- Wastewater treatment and water purification.
- Stabilisation / solidification of industrial wastes.
- Adsorbents for the air sampling of airborne organic contaminants¹⁵.

But there are also more diverse applications including:-

- | | |
|--|-----------------------------|
| • Catalysts. | • Pharmacy. |
| • Catalytic supports. | • Dyes. |
| • Molecular sieves. | • Inks. |
| • Chromatographic applications. | • Paint production. |
| • Fillers and extenders for rubbers. | • Lipsticks. |
| • Sensors, electrochemical and optical devices ¹⁶ . | • Oil well drilling fluids. |

In addition to their potential as adsorbents for pollutants, the utilisation of polycation exchanged clays as catalysts is of particular interest. The remainder of the reported work is concerned with the investigations used to assess the potential of acid-activated polycation exchanged clays as catalysts.

1.3 POLYCATION EXCHANGED CLAYS AS CATALYSTS.

The lack of good crystalline order in sheet silicates is probably the source of their catalytic behaviour, but they also provide a complex array of possible sites for reaction. The structural diversity makes clay catalysts potentially powerful, however, the question remains as to how to maximise the active sites to achieve the greatest efficiency for a given reaction.

Acid treated clays have been used as an effective source of solid protons for a considerable period. Established industrial applications include their use as bleaching earths for the clarification of oils^{17,18,19}, in the production of pressure sensitive carbonless copying paper²⁰ and in synthetic organic chemistry²¹. Their use in petroleum cracking, particularly during the 1973 oil crisis, greatly raised their profile. The organic-exchanged clays were thermally unstable for this application so the inorganic pillared interlayer clays (PILCs) were developed.

PILCs have now become an important family of shape-selective catalysts. These solids combine a tuneable acidity, regular porosity and relatively high thermal stability that makes them similar to zeolite-like materials. The synthesis of different PILCs and their catalytic properties in a variety of chemical reactions have been well researched, however much less information is available concerning the nature of their acid sites.

The acidity of acid centres on various forms of smectites significantly affects their sorption properties^{22,23} and their activity when used as catalyst supports²⁴. Acid dissolution of clays provides useful information on the reactivity of the mineral involved or characteristics of reactants and reaction products. Unfortunately, the studies on acid

dissolution of montmorillonites to date suffer from a non-unified approach with regard to acid type and concentration, treatment times and choice of clay. This makes detailed comparisons difficult.

Understanding of the prepared polycation exchanged clays coupled with the known enhanced catalytic activity of PILCs led to the consideration of the acid-activated polycation exchanged clays (AAPECs) as catalysts for reactions in non-polar media. The activity of the AAPECs was compared to acid treated non-exchanged natural clays and also acid treated tetramethylammonium-exchanged clays. Acid-activated organoclays (AOOCs) which were prepared by co-workers in Bratislava, were also investigated. These acid-activated clays were exchanged with dodecyltrimethylammonium, octadecyltrimethylammonium, or tetramethylammonium cations and exhibited similar activities to PILCs.

Several different clays were considered since it is now generally accepted that clays with different structures are acid leached at different rates. For example, montmorillonites with high magnesium contents in the octahedral sheet are leached more readily than those containing a higher proportion of aluminium. Of particular interest here is the ability to produce hydrophobic catalysts of relatively high acidity using short treatment times.

The chosen test reaction is the acid catalysed transformation of α -pinene to camphene and limonene. Terpenes are industrially significant both for their fragrance properties and because they constitute one of the largest groups of pharmaceutically important natural products²⁵.

1.4 AIMS.

The first aims of the work reported herein were to determine how the type of clay, purification procedures, the nature of the exchange cation, particle size and ionic strength individually affect the adsorption of (poly)cations.

Further aims were to determine the effect of the nature of the clay, the extent of polymer exchange and the nature of the exchange cation on the adsorption of benzene and *p*-nitrophenol and how adsorption compared to that by tetramethylammonium exchanged clays.

Final aims were to determine how the nature of the clay, the extent of acid treatment, the organic exchange ion and the extent of exchange, affect catalytic activity in non-polar media, with the ultimate aim of producing cost-effective, hydrophobic catalysts of relatively high acidity using simple exchange procedures.

CHAPTER 2

Introduction to Clay Minerals.

2. INTRODUCTION.

Clays are naturally occurring minerals which have been used by mankind for thousands of years. Indeed, it is thought that the first living things may have consisted of no more than RNA or RNA-like molecules bound to the surfaces of mineral particles²⁷. Due to their extensive occurrence they were easily found and as long ago as 25,000 years were used in making pots and vessels. Nowadays clays are used in such diverse applications as carriers for drugs²⁸, adsorbents, ion exchangers, catalysts, pharmaceutical additives and fertilisers. Their scientific study however is a much more recent undertaking since their analysis requires techniques which have only been available comparatively recently.

2.1 THE STRUCTURE AND FUNDAMENTAL PROPERTIES OF CLAY MINERALS.

Although the term 'clay' has a precise definition (see below), it can be considered from two standpoints:

1. Particle size.

There is not a particle size that is universally accepted by all disciplines. Most geologists and soil scientists generally use clay minerals that have a particle size of $< 2\mu\text{m}$ when suspended in water. However, sedimentologists generally use $< 4\mu\text{m}$ and colloid chemists use $< 1\mu\text{m}$.

2. Mineralogy.

The product of weathering or volcanic sedimentation.

The term 'clay' has been defined by the Association International Pour L'Étude Des Argiles (AIPEA) nomenclature and Clay Mineral Society (CMS) Nomenclature committees as referring to a naturally occurring material composed primarily of fine-

grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired. Although clay usually contains phyllosilicates, (phyllo = leaf-like), it may contain other materials that impart plasticity and harden when dried or fired. Associated phases in clay may include materials that do not impart plasticity and organic matter^{29,30}.

Their small grain size and variable degree of crystal imperfection, made adequate characterisation of clay minerals extremely difficult prior to the development of modern analytical techniques. Although the first reported investigations were in 1847 by Damour and Salvetat³¹, it was not until the middle of this century that techniques such as electron microscopy, thermal analysis, infrared spectroscopy and particularly x-ray diffraction became available to study clays in detail. It was found that clays were composed of silica, alumina, iron, alkali and alkali earths, but that different clays had different ratios of these components.

2.1.1 The Fundamental Units of Sheet Silicates.

All clay minerals are constructed from two basic units which polymerise into two dimensional layers. These layers then stack to form the layers of a clay particle.

2.1.1.1 Octahedral Sheets.

Individual octahedral units (Figure 1a) polymerise as described above to form the octahedral sheet. These sheets consist of closely packed oxygens or hydroxyls in which Al^{3+} , Mg^{2+} or $\text{Fe}^{2+,3+}$ ions are co-ordinated octahedrally within the lattice (Figure 1b). The hydroxyls are required as a result of bonding between the individual octahedral units. The oxygen atoms gain a negative charge and so must bond to a proton in order to gain charge neutrality.

In this sheet there are three positions for the aluminium or magnesium ions. To achieve charge neutrality there are two possible combinations :-

1. Dioctahedral. Two positions are occupied by trivalent aluminium ions leaving one unoccupied position. This has the formula $\text{Al}_2(\text{OH})_6$.
2. Trioctahedral. All three positions are occupied by divalent magnesium ions. This has the formula $\text{Mg}_3(\text{OH})_6$.

2.1.1.2 Tetrahedral Sheets.

The tetrahedral sheet is formed from very stable silica tetrahedral units, SiO_4^{4-} , (Figure 2a), which polymerise into a two dimensional sheet of chemical composition $\text{Si}_4\text{O}_6(\text{OH})_4$, (Figure 2b). The silicon is at the centre of the tetrahedron and is equidistant from four oxygens, or hydroxyls if necessary to balance the structure. The base of the tetrahedra share three oxygens at the corners and so form a hexagonal network, (Figure 2c).

2.1.1.3 The Formation of Layer Silicates.

The hydroxyl groups from the silicon tetrahedra can be considered to undergo further condensation-polymerisation with the octahedra, (Figure 3). This is possible due to the symmetry and similarity in dimensions of the two different sheets, ($\text{O}-\text{O} = 2.7\text{\AA}$). The different ratios in which these sheets combine, along with the associated exchange cation, gives rise to the difference in properties between the various types of clay and hence is the basis of the classification system for clays.

Condensation of one tetrahedral (T) layer with one octahedral (O) layer results in a structure referred to as 1:1 or T:O. It is also possible to combine a further tetrahedral

layer to the opposite side of the octahedral layer and this results in a 2:1 or T:O:T structure.

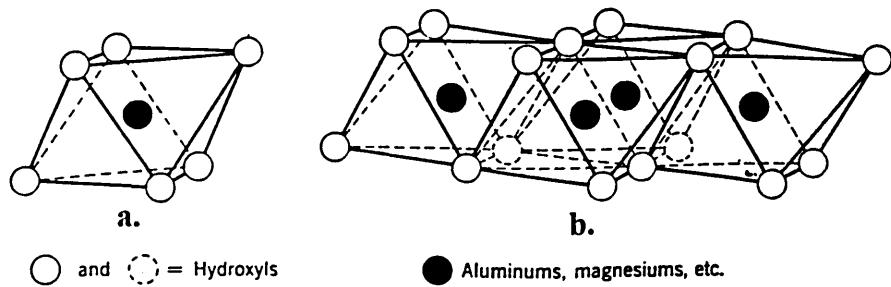


Figure 1. Showing (a) an individual octahedral unit and (b) the octahedral sheet.

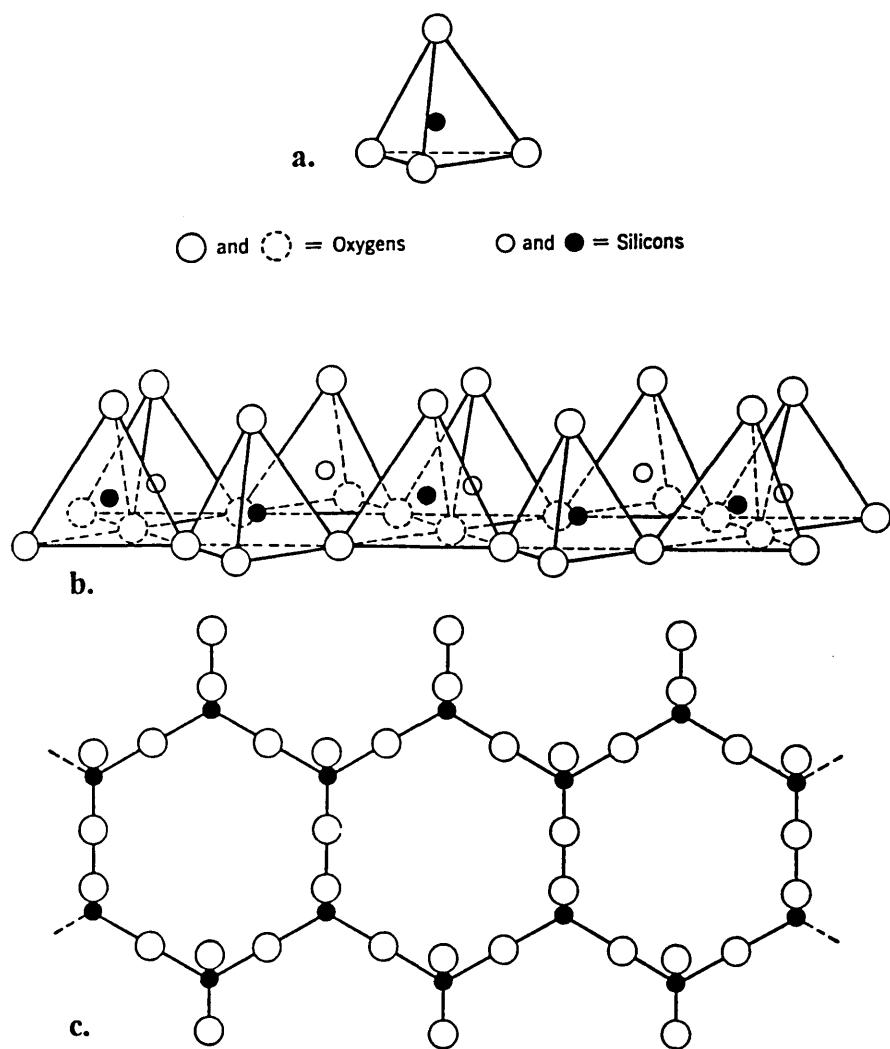


Figure 2. Showing (a) an individual tetrahedral unit, (b) the tetrahedral sheet and (c) the tetrahedral sheet and projection of the hexagonal network.

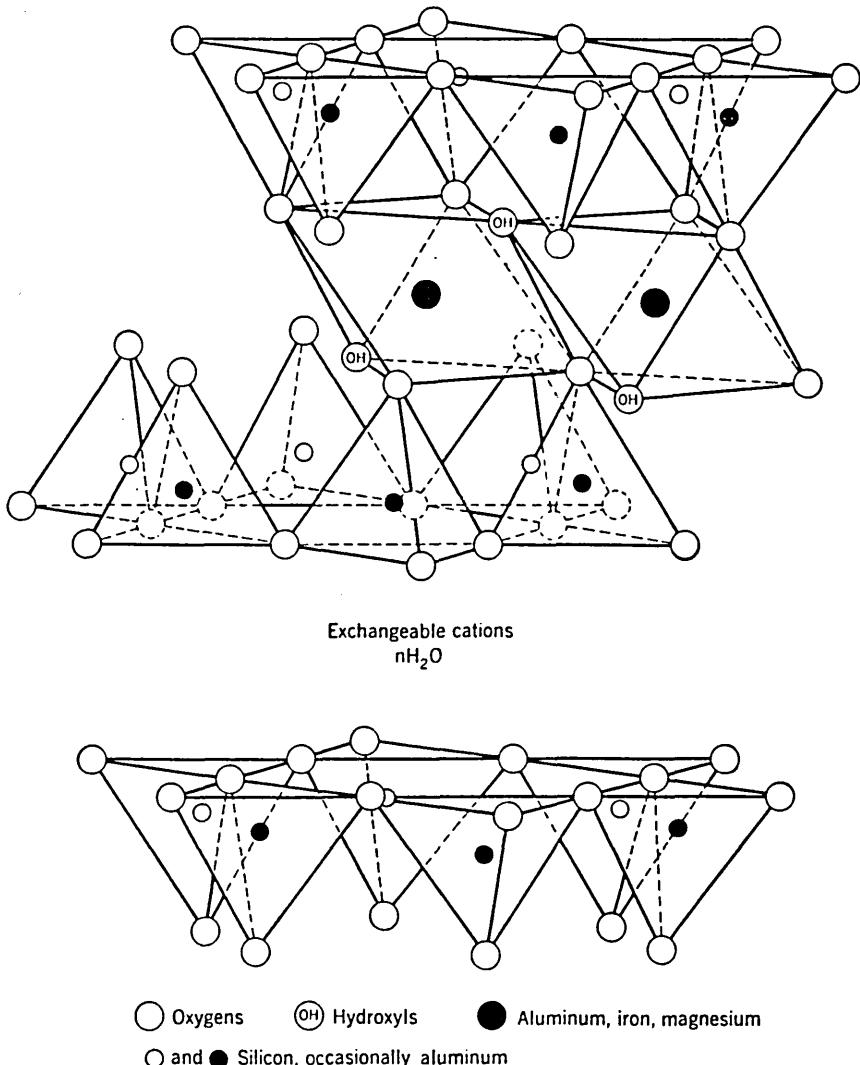
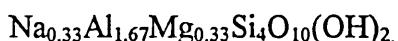


Figure 3. Diagrammatic sketch of the structure of montmorillonite, according to Hofmann, Endell and Wilm³², Marshall³³, Maegdefrau and Hofmann³⁴ and Hendricks³⁵.

2.1.2 Classification.

Clays are commonly described by their chemical formula. Hence, for example, montmorillonite, a clay used in this work, has an idealised formula :



However, for classification purposes, clay minerals are arranged according to

- The type of aluminosilicate layer present, either 1:1 or 2:1.
- The magnitude of the net layer charge.
- The interlayer material that compensates this charge.

Property	Serpentine-kaolin	Talc-pyrophyllite	Smectite	Vermiculite	True (flexible) mica	Chlorite
Layer Type	1:1	2:1	2:1	2:1	2:1	2:1:1
Net Layer Charge	Very low to zero	Zero	Low	Medium	High	Variable
Cation Exchange Capacity (meq/100g)	3 to 15	0	60-120	120-180	~200	10-40
Interlayer Material	None or H ₂ O only	None	Hydrated exchangeable cations	Hydrated exchangeable cations	Non-hydrated monovalent cations	Hydroxide sheet
Isomorphous Substitution	None	None	Occurs readily	Only in tetrahedral sheet	Only in tetrahedral sheet	None
Intercalation Ability	Limited to some polar molecules	None or possibly H ₂ O only	Occurs readily	Occurs readily	None	H ₂ O only
Octahedral Character ^a	(i) Tri (ii) Di	(i) Tri (ii) Di	(i) Tri (ii) Di	(i) Tri (ii) Di	(i) Tri (ii) Di	(i) Tri (ii) Di
Species ^{a,b}	(i) Chrysotile (ii) Kaolinite	(i) Talc (ii) Pyrophyllite	(i) Saponite (ii) Montmorillonite	(i) Tri vermiculite (ii) Di vermiculite	(i) Biotite (ii) Muscovite	(i) Chlinochlore (ii) Donbassite

^aTri = Trioctahedral Di = Dioctahedral, ^bOnly one example is given for each case.

Table 1. The most common groups of clays and their more significant properties.

Each group is then sub-divided on the basis of the octahedral character. 2.5 octahedral cations is the boundary between dioctahedral and trioctahedral. Table 1 lists the most common groups of clays and their most significant properties.

2.2 ADDITIONAL PROPERTIES OF CLAY MINERALS.

In Germany in 1931 several groups began to study clay minerals. The work of Hofmann, Endell and Wilm³² resulted in the first suggested structure for smectites. Modifications by Marshall³³, Maegdefrau and Hofmann³⁴ and Hendricks³⁵ have subsequently been incorporated leading to the structure which is now generally accepted (Figure 3).

A radically different structure for montmorillonite has been suggested by Edelman and Favejee³⁶ in which every alternate SiO_4 tetrahedron in the tetrahedral sheet is inverted. The apical oxygens which now point away from the surface, are replaced by hydroxyl groups which also fill gaps left in the octahedral sheet. It is the dissociation of these groups which was considered to be solely responsible for the cation exchange capacity. McConnell³⁷ has also suggested that $(\text{OH})_4$ units occasionally replace silica tetrahedra. It was later found, however, that the dissociation of apical hydroxyl groups did not account for the observed cation exchange capacities of montmorillonites. Hence this model was modified to one in which only 20% of the tetrahedra were inverted. In this case 80% of the cation exchange capacity would arise from exchange of protons from the exposed hydroxyl group. This is thought unlikely and is one of the main arguments against the Edelman and Favejee model. Also, their model would make the cation exchange capacity pH dependent and this is not the case.

2.3 CATION EXCHANGE CAPACITY (CEC).

Clay materials contain water-soluble salts which may have been entrained in the clay at the time of accumulation or may have developed subsequently as a consequence of ground water movement and weathering, or other processes. The clay minerals and some organic material found in clay materials may also carry adsorbed cations and anions which are exchangeable for other ions by simple treatment, usually an aqueous solution. This sorption from solution is normally considered as a simple exchange process. If the raw clay is placed in a solution of a different ion then a stoichiometric ion exchange can occur. In non-selective sorption the amounts of cations sorbed are proportional to their relative concentrations in solution and their sorption can be described by the laws of mass action. Certain cations are, however, sorbed more selectively than others and are held more tightly against replacement by other cations. K^+ , NH_4^+ , and other large monovalent cations are sometimes held so strongly that they are said to be fixed. This is discussed further in Section 2.3.5.

The physical properties of clay materials depend to some extent on the nature of the adsorbed exchangeable ions carried by the clay mineral components. Hence, a sodium clay is likely to have different plastic properties to one containing calcium. This difference will be great or small depending on the CEC of the clay. Also, the relative abundance of the adsorbed ions present is important in determining its properties. The fact that adsorbed ions can significantly alter the properties of a clay provides a possible way of altering those properties to suit a particular function. This capacity for ion exchange can be measured and is described in terms of milliequivalents of each cation per gram, or more usually per 100 gram i.e. meq/100 g³⁸.

2.3.1 Determination of CEC.

CEC is generally understood to be equivalent to the layer charge, which is a constant value. Hence, CEC is considered a material constant for the clay, assuming there is negligible contribution from broken bonds. There are a number of methods used for determination of the CEC including, the adsorption of Co(II)³⁹, surface tension measurements⁴⁰, colourimetric titration by hexaminocobaltichloride⁴¹, methylene blue and crystal violet methods⁴², ‘staining’ by Cs⁺ for electron microscopy⁴³ and barium exchange methods⁴⁴. Arguably the most widely used method is via complete ion exchange with ammonium acetate. The uptake of this can be measured by Kjeldahl nitrogen analysis to give an indication of the cation exchange capacity^{45,46}.

It should be noted that the measured cation exchange capacity is only equivalent with the layer charge if all compensating cations are accessible for exchange

It has been found that this charge density is not distributed evenly among the clay layers⁴⁷. This means that if the clay contains a number of cations, some particles will contain one specific cation while other particles will contain another. Since many properties of clays are related to the interlayer cations this phenomenon - known as layer charge heterogeneity - is important.

There are a number of contributors to the magnitude of the CEC and the type of clay will determine which is the most significant.

2.3.2 Isomorphous Substitution.

Octahedral and tetrahedral cations may be substituted by other elements of an appropriate size. This phenomenon is responsible for some important properties of clay minerals. In smectites this accounts for approximately 80% of the total CEC and is as a result of substitution of Si⁴⁺ for Al³⁺ in the tetrahedral sheet and of e.g. Mg²⁺ or Fe²⁺ for

Al^{3+} in the octahedral layer. Since substitution of higher valent by lower ions occurs most commonly, this results in the initially neutral clay sheet gaining a net negative structural surface charge. This is balanced by exchangeable cations at, or near, the silicate surface. In nature the exchangeable cations are usually alkali or alkali earth metals such as Na^+ or Ca^{2+} and may be hydrated or not. The majority of isomorphous substitutions are in the octahedral layer. This effect will be pH independent.

2.3.3 Broken Bonds.

Edge surfaces of clay particles carry charges due to the presence of broken bonds. In smectites this accounts for approximately 20% of the total CEC. Broken bonds around the edges of silica-alumina units give rise to unsatisfied valences which are balanced by adsorbed counter-ions. The number of broken bonds, and hence the CEC due to this factor, increases as the particle size decreases.

2.3.4 The Hydrogen of Exposed Hydroxyls.

This is thought to account for the remaining CEC not covered by the above factors. If the exposed hydroxyl groups are ionised the result will be a negative charge on the oxygen and an exchangeable hydrogen ion. However, the hydrogen is likely to be very tightly bound and difficult to replace by a sterically larger cation. This effect will be pH dependent.

2.3.5 Exchangeable Ions and Soluble Salts.

The sites that the exchangeable cations occupy within the interlayer of clay, depends to a large extent on the hydration state of the clay. In smectites the amount of interlayer water may be changed according to the cations present and to the ambient physical conditions. A particular feature of hydrated smectites is the readiness with which exchange of interlayer cations can occur. If the clay is anhydrous small exchange cations may occupy the hexagonal cavity in the tetrahedral sheet. As water begins to be

adsorbed by the clay, the cation is displaced from the hexagonal cavity and lies within the water layers which are now in contact with the basal surface of the clay. Hence, the interlayer water solvates ions such as Li^+ , Ca^{2+} and Na^+ and makes them mobile within the interlamellar space. Conversely, the interaction of K^+ ions with the clay layers is so energetically favourable that the ion will not hydrate in the presence of water. As a result clays that contain predominantly K^+ ions (e.g. micas) do not swell in water or other polar solvents. It is also very difficult to exchange K^+ ions for other cations.

Selective sorption of K^+ , and also NH_4^+ and Cs^+ ions by clays has been observed by a number of investigators^{48,49,50}. Although fixation of K^+ and NH_4^+ ions by clay minerals had earlier been attributed to their close fit within the hexagonal cavities of basal oxygen planes^{51,52}, low hydration energy of the ions is now considered to be the major factor in cation selectivity and fixation⁵³. Data showing greater sorption and fixation of Cs^+ and Rb^+ ions with smaller hydration energies than that of K^+ ions can be similarly explained.

Cations with a low hydration energy such as K^+ , NH_4^+ , Rb^+ and Cs^+ produce interlayer dehydration and layer collapse and are therefore fixed in interlayer positions. Conversely, cations with a high hydration energy such as Ca^{2+} , Mg^{2+} and Sr^{2+} produce expanded interlayers and are not fixed⁵⁴.

The replaceability of cations associated with the clay by cations of a chosen type depends on a number of factors, namely:

- The nature of the clay mineral.
- The nature of the cation, i.e. hydration energy, valency, size.
- The electrolyte concentration in which the cation exchange will take place.
- The population of exchange sites on the clay.

Although the replaceability of exchange cations can be difficult to predict, it is now generally accepted that the replacing power of cations follows the series $\text{Li}^+ < \text{Na}^+ < \text{K}^+$

$< \text{Mg}^{2+} < \text{Ca}^{2+} < \text{H}^+$. Generally, ions of higher valency replace those of lower valency and are also bound more tightly to the interlayer exchange sites. In the case of ions of the same valency competing for the same sites, it is generally the larger ions that are better at replacing smaller ions, until their size exceeds that which can be accommodated by the hexagonal cavities. Hydrogen ions are the most significant exception to this rule since H^+ behaves like a slightly hydrated di- or trivalent ion.

2.4 CATION MIGRATION.

A further noticeable property is the mobility of the interlayer cations in the clay structure. As mentioned above, (Section 2.3.2), when isomorphous substitution occurs the clay layer carries a net negative charge which is compensated by exchangeable cations. However Hofman and Klemen⁵⁵ among others have shown that small ions such as lithium or a proton can diffuse into the layer and reside in unfilled octahedral positions following heat treatment of 150-300°C. This leads to a sharp reduction in cation exchange capacity and so provides a relatively simple yet effective method of controlling the cation exchange capacity and perhaps the charge density of a clay.

2.5 THE HYDRATION AND SWELLING OF CLAY MINERALS.

Swelling of clay minerals is possible because the parallel lamellae in these structures are bonded by van der Waals and electrostatic forces rather than covalently. In smectites such as montmorillonite or hectorite the charge density on the sheets is low and the structure swells rapidly by penetration of polar species between the sheets⁵⁶. Montmorillonite is able to adsorb water to a greater extent than many other clays because water is not only adsorbed on the external surfaces but also in the interlamellar space.

Smectite minerals can swell in one of two very different ways^{57,58}.

1 Crystalline swelling.

This is caused by the hydration of the exchangeable cations in the interlayers. In concentrated brine, or in a solution dominated by divalent or multivalent cations, smectites experience only a small volume increase or swelling. In these solutions, water molecules are structured in layers on the clay surface. This type is called crystalline swelling.

2. Osmotic swelling.

This results from the large difference between ion concentration close to the clay surface and in pore water. The essential features of osmotic swelling are not only the large spacings observed between individual clay layers but also the different nature of the forces between the layers. These forces are osmotic and result from a balance of electrostatic forces, van der Waals forces and the osmotic pressure exerted by the interlamellar cations, i.e. in dilute solutions where Na^+ is the dominant cation, smectites experience a large volume increase or swelling. In these solutions, an electrical double layer will develop on the clay surface and cause a strong repulsion between the clay platelets. Hence, osmotic swelling is much more damaging in structures such as hydrocarbon reservoirs than crystalline swelling.

When less than three molecular layers of water are present in the interlamellar region, the structure of sorbed water on smectites has been shown to be influenced predominantly by the exchangeable cations^{59,60}. Spectroscopic investigations of smectite-water interactions^{61,62} suggest that two distinct environments of sorbed water are present:

1. Water molecules co-ordinated directly to exchangeable metal cations.
2. Physisorbed water molecules occupying interstitial pores, interlamellar spaces between exchangeable cations, or polar sites on external surfaces.

In the latter case, water is not strongly bound to the clay surface and these molecules are selectively removed during the desorption process. Upon dehydration, the more labile water is removed from the interlamellar region, leaving water molecules that are co-ordinated to the exchangeable metal cations and thus reducing intermolecular interactions between water molecules. In addition, the remaining water molecules are polarised by the exchangeable cation

Swelling characteristics of clay minerals can be quantified by x-ray diffraction (XRD) analysis since clay swelling is a result of the increase in interlayer spacing (d_{001} spacing) in clay particles⁶³.

The sorption of water by clays is governed by the nature of the saturating cation and by the value and the localisation of layer charge of the adjacent silicate sheets. As discussed above, the net negative charge on smectite clays that arises as a result of isomorphous substitution is neutralised in nature by organic cations such as Na^+ or Ca^{2+} on the clay interlayers and external surfaces. It has also been shown that for a given interlayer cation (Li^+ , Na^+ , K^+ , Mg^{2+} or Ca^{2+}) and for a given octahedral composition (Mg^{2+} , Fe^{2+} , Al^{3+} or Fe^{3+}), the hydration energy generally increases with the layer charge so that most of the minerals of high charge are hydrophilic and should hydrate spontaneously in water⁶⁴.

Hydration of the interlayer cations in the presence of water initiates a separation of the clay layers causing a separation of the clay (Figure 4). In smectites exchanged with monovalent cations having high hydration energies (e.g. Na^+ or Li^+) the individual clay platelets may become completely separated in the presence of water⁶⁵.

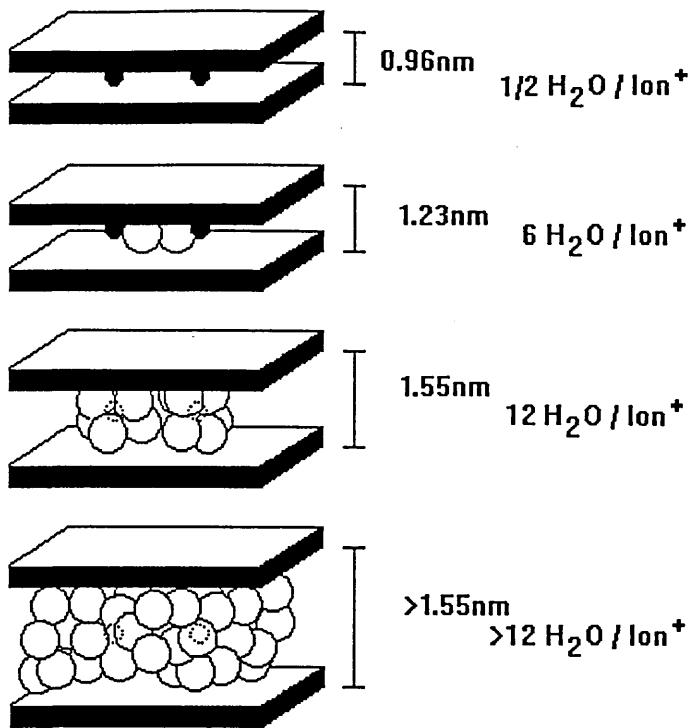
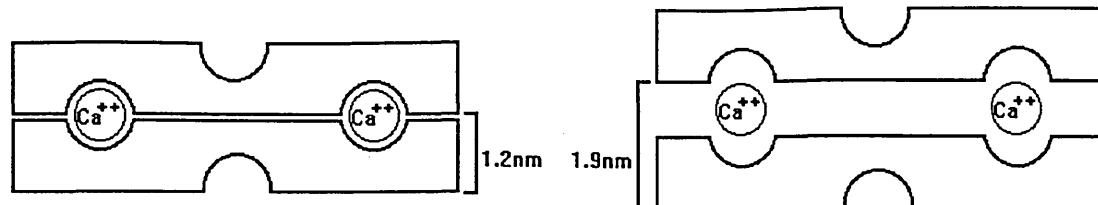
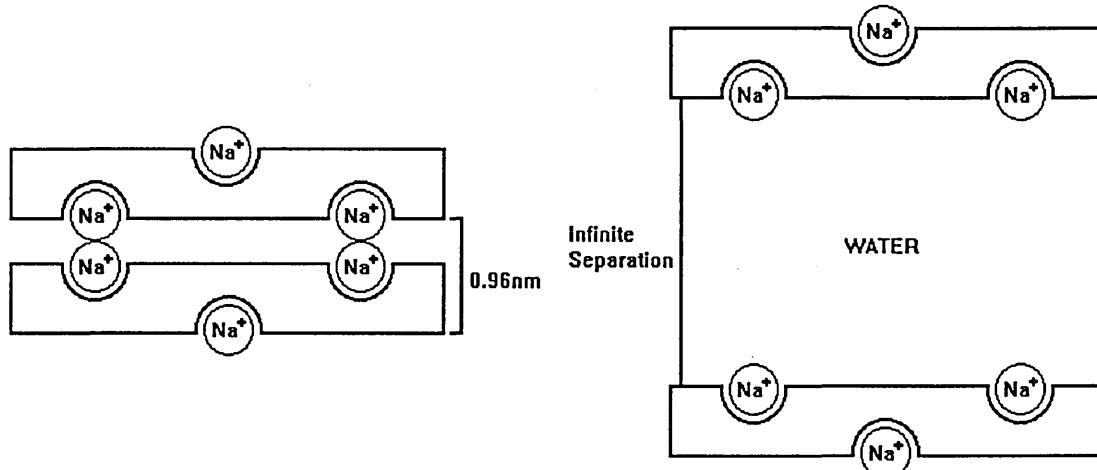


Figure 4. Showing the swelling of montmorillonite in water.

Swelling occurs in a series of discrete steps, corresponding to the intercalation of 0, 1, 2, 3 or 4 layers of water molecules⁶⁶. Norrish⁵⁷ showed that the layers of sodium exchanged montmorillonite could be expanded stepwise by the addition of water layers. He observed both the initial stepwise swelling of smectites up to 20 Å and an increase in basal spacings > 40 Å that varied linearly with the inverse square root of the electrolyte concentration. Above 40 Å the layers are taken to be completely disassociated. He found that the d_{001} spacing for anhydrous sodium exchanged montmorillonite was 9.6 Å (0.96 nm), which increased to 15.5 Å (1.55 nm) for the two-layer hydrate. This series is markedly different to the divalent cation exchanged smectites where the maximum distance between individual clay layers is approximately 19 Å (1.9 nm). Divalent cations, such as Ca^{2+} must associate with charge deficient areas on two clay sheets to achieve charge neutrality, whereas a monovalent cation such as Na^+ can associate with a charge deficient area on just one. Hence, when hydrated, single sheets predominate with the monovalent system, compared to a reduced d_{001} spacing and therefore reduced surface area in the divalent system (Figure 5).



a.



b.

Figure 5. a. Showing how divalent cations associate with two different clay platelets, resulting in a small basal spacing upon hydration.
 b. Showing the expansion to infinite separation of Na-montmorillonite upon hydration.

Hence the swelling of smectites can be controlled by varying electrolyte concentration. Slade *et al.*⁶⁷ investigated the swelling of smectite samples in concentrated NaCl solutions in relation to layer charge. They found that except for the most highly charged smectites, an expansion from ≈ 15.5 to ≈ 18.5 Å occurred as the NaCl concentrations were reduced. This expansion corresponds to the transition from two to three sheets of water between the silicate layers.

It follows then the nature of the exchange cation and the electrolyte concentration will affect the interparticle association of clay suspensions and this will now be discussed.

2.6 INTERPARTICLE ASSOCIATIONS.

2.6.1 Electrical Phenomena at Interfaces.

Across any interface separating two phases there is, in general, a difference in potential. This potential difference may be pictured as an electrical double layer. One phase acquires a net negative charge and one acquires a net positive charge. Such double layers exist not only at plane surfaces but also around solid particles, such as clays, suspended in a liquid medium. Stern (in van Olphen³⁸) proposed that the charge on the solid is rigidly fixed and on top of this there may be a practically immobile layer of oppositely charged particles of liquid. Further out from the surface there is a diffuse layer of charge, which may have a sign either the same as or opposite to that of the adsorbed layer. This diffuse layer is free to move, for example under the influence of an applied potential difference. The potential drop in the diffuse layer is known as the zeta potential⁶⁸ (Figure 6).

The types of aggregates that form in clay suspensions result from the state of balance between:

1. van der Waals attractive forces which are responsible for the attraction between clay platelets. If these forces dominate then flocculation may occur, however, interparticle forces are inversely proportional to the seventh power of the distance. These forces are essentially unaffected by electrolyte concentration.
2. Electrostatic repulsive forces that exist between the clay double layers which have negative charges as a result of isomorphous substitution. These forces decrease with increasing electrolyte concentration.

Therefore, changes of the physico-chemical conditions of the system result in a change in the balance of these forces, which result in changes in the type of aggregate⁶⁹. Among different chemical factors, the kind and concentration of electrolyte and the pH exert the greatest influence on the type of microstructure⁷⁰.

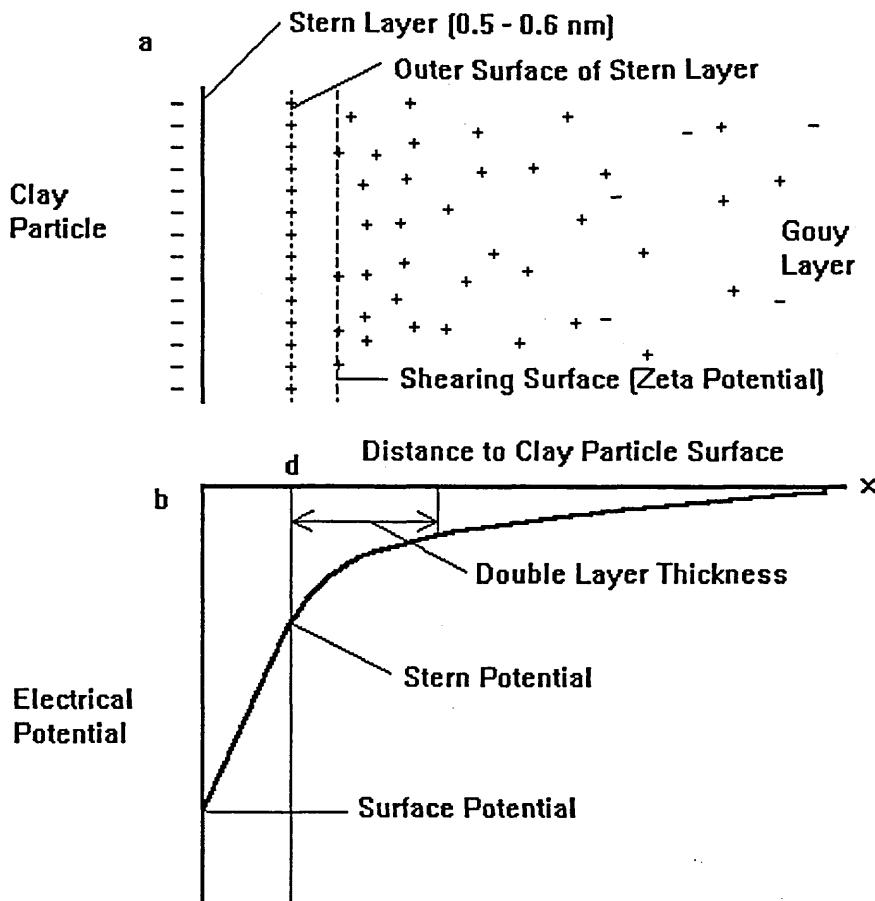


Figure 6. Showing the Stern-Gouy electrical double layer. (a) Charge distribution as related to distance, (b) potential distribution as related to distance. The x scale from the origin to d is exaggerated approximately 3 times for clarity.

2.6.2 Interparticle Associations in Clay Suspensions.

The significance of the exchangeable cation has already been discussed (Section 2.3.5). However, these cations are also primarily responsible for the stability of clay suspensions. van Olphen⁷¹ carried out rheological studies of homo-ionic suspensions of sodium montmorillonite and showed significant changes in suspension viscosity as a result of increasing NaCl concentrations. The changes result from deflocculation⁷² and aggregation⁷³. For smectite platelets in aqueous suspension there are three possible modes of particle association (Figure 7)⁷⁴.

1. Association between an edge surface and a siloxane planar surface, edge-face (E-F).
2. Association between edge surfaces of neighbouring particles, edge-edge (E-E).
3. Association between siloxane planes of two parallel platelets, face-face (F-F).

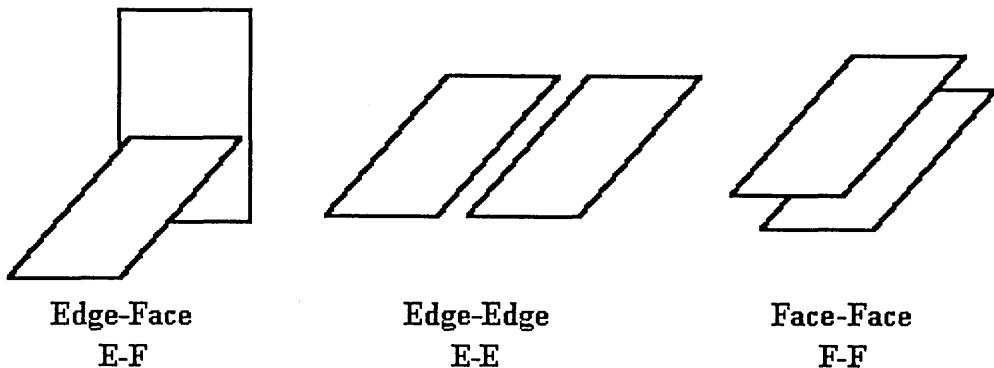


Figure 7. Showing the three basic modes of particle association.

In highly dilute suspension only a few flocs form which do not have sufficient mass to sediment out of solution. But, as the electrolyte concentration increases, the double layers at both the negative basal surface and positive edge sites are compressed and at the critical flocculation concentration (CFC) both E-F and E-E associations can occur. As the electrolyte concentration increases further the F-F associations can occur and 'oriented aggregates' are formed⁷⁵. These aggregates have sufficient mass to readily sediment out of solution and flocculation is observed.

In summary, the interparticle associations give rise to three different suspensions:

1. Deflocculated Suspensions.

An overall repulsive force between clay platelets results in particles being well dispersed or peptised (Figure 8a). If each particle is given a similar charge the suspension can be made to peptise.

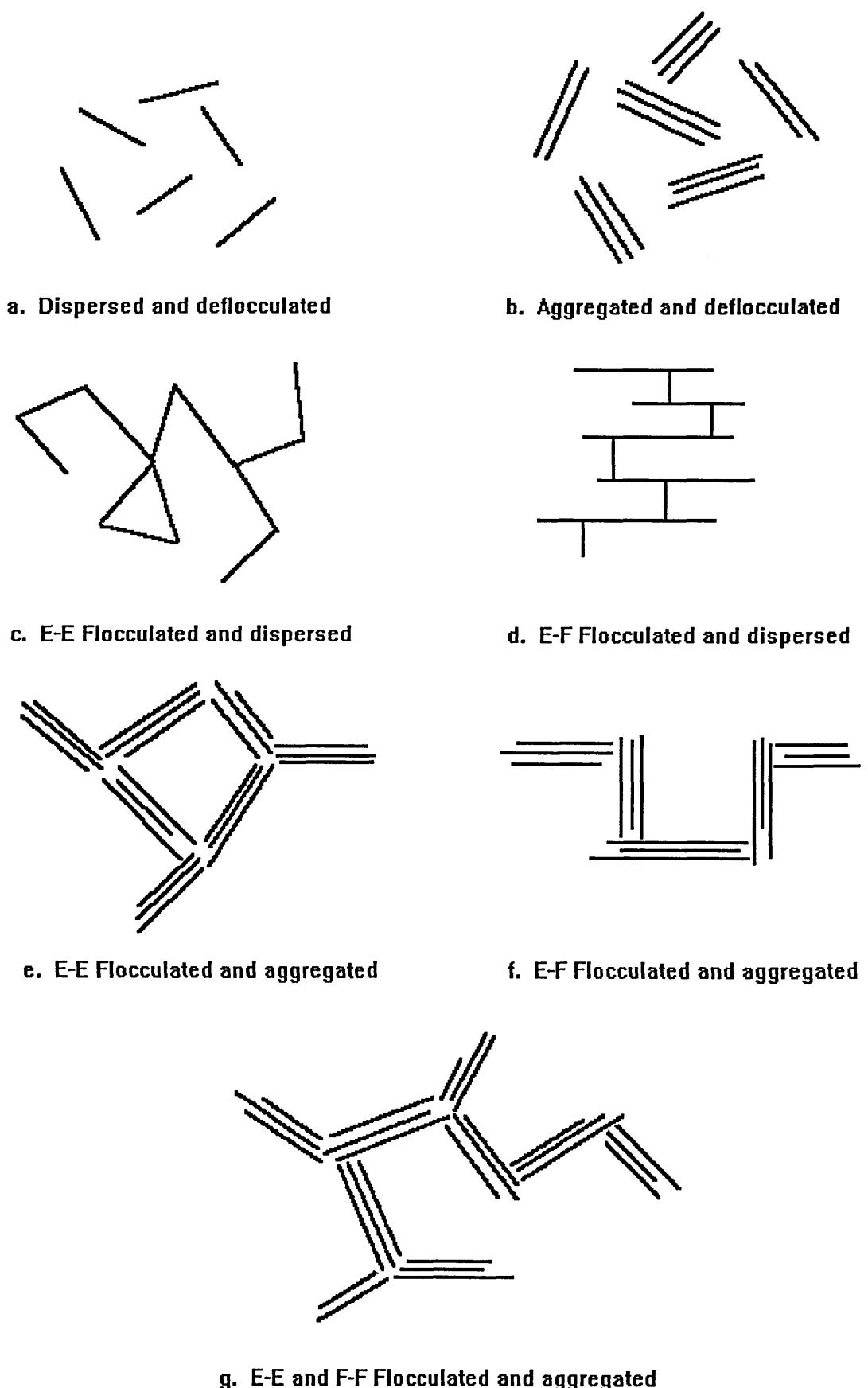


Figure 8. Showing clay particle associations in different types of suspension.

2. Flocculated Suspensions.

E-E (Figure 8c) and E-F (Figure 8d) bonds form as a result of a net attractive force between the clay platelets. ‘Flocs’ form in dilute suspensions. A rigid ‘card-house’ structure forms in concentrated suspensions (Figure 8d).

3. Aggregated Suspensions.

A dominance of F-F associations, as a result of clay plates stacking one upon the other, leads to an aggregated system. The stacked sheets may be disaggregated by mechanical sheer forces or further hydration. The aggregates themselves may form E-E (Figure 8e) and F-F type (Figure 8f) associations and be deflocculated (Figure 8b) or flocculated (Figure 8e, f and g).

2.6.2.1 Controlling Flocculation of Clay Suspensions.

Flocculation can also be controlled by the addition of polymers and certain organic cations and by controlling the nature of the exchange cation associated with the clay. As discussed above (Section 2.3.5), predominantly polyvalent cation exchanged clays are more flocculated because of the association between the cation and more than one exchange site on more than one clay platelet. Hence, to deflocculate a polyvalent cation exchanged clay, the resident cations must be replaced by monovalent ones. It has been shown that tactoid sizes (with the number of plates per tactoid relative to Li⁺ exchanged montmorillonite), increased in the order Li⁺ < Na⁺ < K⁺ < Mg²⁺ < Ca²⁺, varying from 1.5 for Na⁺ to 6.1 for Ca²⁺ exchanged montmorillonite, i.e. a suspension of Ca²⁺ exchanged montmorillonite will be more flocculated than a Li⁺ exchanged montmorillonite suspension⁷⁶.

2.6.2.1.1 Face Charge Reversal.

Upon the addition of certain organic cations, e.g. long chain quaternary ammonium salts, the double layer of the clay platelet is suppressed leading to flocculation in the system.

Upon further addition, the hydrocarbon chains of the adsorbed cation, which are pointing towards the solution, are attracted by van der Waals forces to the hydrocarbon chains of the newly added salt. Hence the cationic groups of the second layer now point towards the solution and a positive particle is formed⁷⁷. This is not an economically practical method of reversing the net negative charge on the face of clay platelets since large quantities of cations are required.

2.6.2.1.2 *Edge Charge Reversal.*

A more economically viable option of controlling flocculation is the addition of small amount of salts containing large polyanions, such as polyacrylate or silicate. These anions are chemisorbed at the positive sites on the edges of broken octahedral sheets thus making the edge sites negatively charged. These sites represent only a small percentage of the total surface area and so only a small quantity of salt is required.

An alternative method of edge charge reversal is to raise the pH of the clay suspension above pH 8.0. This will increase the number of negative silic acid groups on the platelet edges.

2.7 ACIDIC PROPERTIES OF CLAYS.

The surface acidity of a clay mineral is responsible for many of its colloidal properties, its readiness to be dispersed in various media and its ability to adsorb different ions and molecules. The catalytic activity of different clay minerals, which is very important for many natural and industrial processes, is determined by their surface acidity. Acidic and basic sites of different natures and with different strengths, appear together on the clay surface, and they determine the bulk acidity of the mineral.

The term ‘surface acidity’ is widely used to refer to the ability of layer silicates to act as Brønsted acids i.e. to donate protons to adsorbed bases. This term can be misleading since, strictly speaking, the oxygen surface of the silicate layers has a basic character

since it is rich with lone-pair electrons^{78,79}. Oxygen planes of clay minerals are formed by a continuous linkage of $[\text{SiO}_4]^{4-}$ tetrahedra. A d(π)-p(π) bond exists between oxygen and silicon atoms in Si-O-Si and Si-O-Al groups. Partial π interactions between oxygen and silicon causes the oxygen atom to serve as a weak base. The acid properties are, in fact, derived from the ionisation of the adsorbed water molecules associated with the exchangeable cations or, to a lesser extent, with the silicate surface. Water associated (or co-ordinated) with interlayer cations is known to be acidic since it can dissociate to yield protons under the polarising influence of the cation. Hence, the acidity of this water increases with an increase in the polarising power of the exchangeable cation, in the order of $\text{K}^+ < \text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$ ⁸⁰.

The basicity of clay minerals is affected by isomorphous substitution (Section 2.3.2). Tetrahedral substitution of Si^{4+} for Al^{3+} leads to changes in the clay surface properties, resulting from an increase in the basic strength of the siloxanes. Substitution of Mg^{2+} or Fe^{2+} for Al^{3+} in octahedral sheets increases the polarisation of the OH planes.

CHAPTER 3

Review of the Interactions of Clay Minerals With Organic Compounds.

3. INTRODUCTION.

It was in the 1940s, when it was realised that montmorillonite adsorbed organic compounds, that the interest in the interaction between clays and organic compounds began. One of the main driving forces was the realisation that certain organic compounds, particularly polymers, when added to soils greatly improved the soil structure.

The adsorption and intercalation of organic molecules by smectites is a subject that has attracted much attention since the work of Hofmann *et al.*⁸¹ and Smith⁸² in the mid 1930s. Much of this work has centred on examining the intercalation of different organic species and how they interact with the clay surface. In order to achieve intercalation it was often necessary to treat the smectite with pure organic material either as a liquid or a vapour.

In recent times environmental pressures have resulted in a growing interest in studying the adsorption of organic species, particularly toxic materials, from solution in water or in organic solvents. This effort has shown that for many organic molecules, particularly non-polar or weakly polar ones, the adsorption on untreated smectite surfaces is small. This is because, as discussed in Chapter 2, in the natural or untreated state, the negative charge of clays is usually balanced by inorganic exchangeable ions such as sodium and calcium, which are strongly hydrated in the presence of water. The hydration of these exchangeable metal ions imparts a hydrophilic nature to the mineral surfaces. As a result the adsorption of non-polar hydrocarbons by clays is suppressed in the presence of water because relatively non-polar organic molecules cannot effectively compete with highly polar water for adsorption sites on the clay surface.

In order to modify the natural hydrophilic character of natural clays, charged organic molecules have been exchanged in the interlamellar space of clay minerals since the 1940s, yielding the so-called 'organoclays'. The organic molecules include small chain organocations, e.g. tetramethylammonium cations, and also organocations with longer alkyl chains, e.g. hexadecyltrimethylammonium cations. Small organic molecules can act as 'props' which hold the aluminosilicate surfaces permanently apart and increase the already significant surface area of clays. Alternatively, the alkyl chains of larger organic molecules fill the interlayer space. In general, larger basal spacings yield greater surface areas and available porous volumes. In the modified form, the clay surface may become organophilic and interact strongly with organic vapours and with organic compounds dissolved in water. Much of the literature has been concerned with organoclays derived by exchange with quaternary ammonium cations (QACs). Research leading to the development of organoclays will now be discussed.

3.1 MECHANISMS OF THE INTERACTIONS OF CLAY MINERALS WITH ORGANIC COMPOUNDS.

Clays interact with many organic compounds to form complexes of varying stabilities and properties. The adsorption of organics on clay minerals can occur by any one of a number of mechanisms depending on the nature of the clay, and the adsorbed organic compound. Organic cations are adsorbed by an exchange reaction but may be assisted by hydrogen bonding, coordination/ion dipole, protonation and physical forces depending on:

- The structure (molecular weight, chain length etc.) of the organic molecule.

- Functional groups present in the organic molecule such as hydrophobic groups (-C-C-C-C-), positively charged groups (-NH_3^+), negatively charged groups (-COO^- , phenolate, -SO_3^-), electronegative groups, (-C=O , -C-O-C- , -OH) or π bonds (-C=C- , aromatic rings).
- Configuration of the organic cations.
- The composition of the aqueous phase present.

The exchanged organic ions affect the adsorption behaviour of the clay in a way that appears to be related to the size and molecular arrangement of the exchanged organocation in the clay⁸³. Exchange with organic cations significantly reduces the hydration of the clay and concomitantly decreases the ‘free’ aluminosilicate area, i.e. the surface not covered by the organic exchange ions. As a result the surface properties of the clay may change considerably from highly hydrophilic if the clay contains mainly inorganic cations, to increasingly organophilic as the inorganic cation is progressively replaced by the organic cation. Depending on the size or hydrophobicity of the organic cation, two types of organoclays can result.

3.1.1 Organophilic Clays.

These are generally of the type $[(\text{CH}_3)_3\text{-NR}]^+$, or $[(\text{CH}_3)_2\text{-NR}_2]^+$ where R is a large alkyl group ($>\text{C}_{10}$), such as hexadecyltrimethylammonium, (R is $-(\text{CH}_2)_{15}\text{CH}_3$), or aromatic hydrocarbon. The large organic groups form a partition medium giving rise to a particularly effective clay-complex for the adsorption of organic contaminants. The partition phases are compositionally and functionally similar to bulk phase hydrocarbon solvents such as hexane or octanol, except that here the organic partition phase is fixed

on the clay surfaces. As the alkyl chain length, and hence the organic content of the exchange cation decreases however, the uptake of organic species from water also decreases.

3.1.2 Adsorptive Organoclays.

Here the exchange organic cation is small, e.g. tetramethylammonium, and exists as discrete entities on the clay layers. The ions do not form partition phases, rather the exchanged clay behaves as a solid surface adsorbent. The surfaces of these clays can be viewed as containing isolated quaternary ammonium exchange cations that are separated by 'free' (uncovered) planar aluminosilicate mineral surfaces⁸⁴.

3.2 TERMS OF ABBREVIATION.

Hereafter, exchanged clays will be described thus:

Montmorillonite exchanged with a cation of interest X will be abbreviated by X-montmorillonite. Hence, for montmorillonite exchanged with TMA⁺ ions, X=TMA⁺, and the resultant complex is therefore designated TMA-montmorillonite.

3.3 ADSORPTION ISOTHERMS.

Nernst first studied the partition or distribution of a solute between two immiscible solvents (discussed in Bromberg⁸⁵). Generally the partition coefficient, which is the ratio of the concentrations of the solute in the two solvents, is a constant. The partition mechanism has been extended to describe the sorption of solutes on clay minerals and soil materials for systems in which no specific bonding was involved.

Early researchers established that the sorption of nonionic, toxic organic molecules from aqueous solutions could be correlated with the total organic content of the adsorbent^{86,87,88}, indicating that the adsorption process is one of partition into the organic component of the adsorbent. However, more recent studies suggest that many exceptions may exist. Hence, two types of partition mechanisms have been proposed.

1. Earlier Greenland *et al.*^{89,90}, Theng⁹¹ and Theng and Scharpenseel⁹² proposed that the linear sorption isotherm observed with clay minerals can be characterised by a partition of a solute between the bulk and intercrystalline water.
2. Later Chiou *et al.*^{93,94}, proposed that the sorption of neutral organic chemicals is essentially a partition process between the soil organic matter and soil water.

More recently, Lee *et al.*¹¹, Smith *et al.*⁹⁵ and Jaynes and Boyd⁹⁶ attributed this latter mechanism to the enhanced sorption of neutral organic molecules on soils and clays exchanged with organic cations with one or more long alkyl groups. Since clay minerals saturated with metal cations contain negligible amounts of organic matter, the sorption of neutral organic molecules on these clays only involves the partition mechanism proposed by the earlier investigators.

The nature of the partition mechanism will generally result in one of three different adsorption isotherms⁹⁷ (Figure 9):

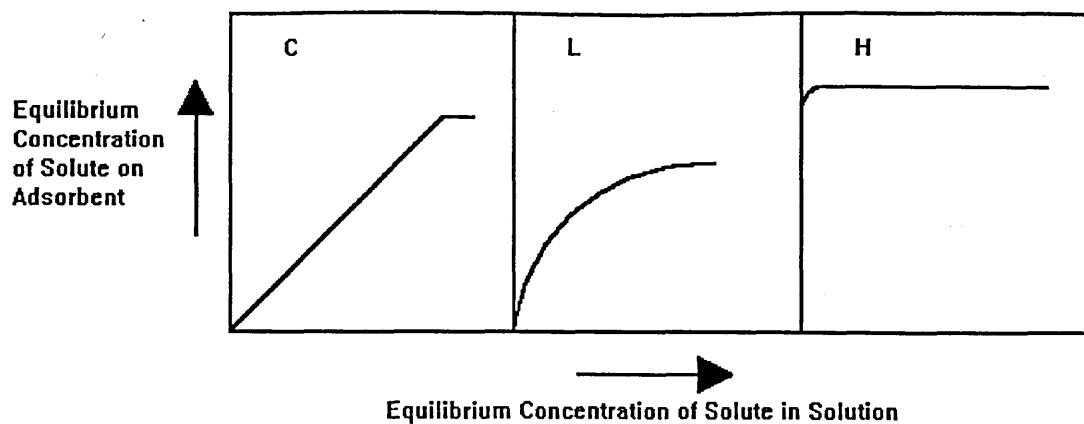


Figure 9. Showing the three most common isotherm types, Linear (C), Langmuir (L) and High Affinity (H).

1. Linear.

If partition of molecules between two phases e.g. of alcohol molecules between bulk and interstitial water, is constant then the resulting isotherms would be expected to be of the 'C' or linear type.

2. Langmuir.

Langmuir type isotherms are obtained when the partition process is either concentration-dependant or other factors are involved.

3. High Affinity.

'H' or high-affinity isotherms, e.g. for diquat adsorption, are characterised by a region in which all the added herbicide is adsorbed, followed by a short shoulder in which the extent of adsorption is related to the herbicide concentration in solution. This finally reaches a plateau approaching the exchange capacity of the adsorbent for which the amount taken up is little influenced by the solution concentration.

The initial slope (Figure 9) may be regarded as, for example in clay-solute systems, a measure of the ease with which solute molecules can find vacant sites on the surface.

3.4 ORIGIN AND DEVELOPMENT OF ORGANOCLAY COMPLEXES.

Name of ion	Abbreviation	Type	R
Tetramethylammonium	TMA ⁺	$[(\text{CH}_3)_3-\text{NR}]^+$	-CH ₃
Tetraethylammonium	TEA ⁺	$[(\text{C}_2\text{H}_5)_3-\text{NR}]^+$	-CH ₂ CH ₃
Tetrapropylammonium	TPA ⁺	$[(\text{C}_3\text{H}_7)_3-\text{NR}]^+$	-(CH ₂) ₂ CH ₃
Trimethylphenylammonium	TMPA ⁺	$[(\text{CH}_3)_3-\text{NR}]^+$	-C ₆ H ₅
Nonyltrimethylammonium	NTMA ⁺	$[(\text{CH}_3)_3-\text{NR}]^+$	-(CH ₂) ₈ CH ₃
Hexadecyltrimethylammonium	HDTMA ⁺	$[(\text{CH}_3)_3-\text{NR}]^+$	-(CH ₂) ₁₅ CH ₃
Dioctadecyldimethylammonium	DODMA ⁺	$[\text{CH}_3)_2-\text{NR}_2]^+$	-(CH ₂) ₁₇ CH ₃
Decyltrimethylammonium	DTMA ⁺	$[(\text{CH}_3)_3-\text{NR}]^+$	-(CH ₂) ₉ CH ₃
Decyltrimethyldiammonium	DTMDA ⁺	$[(\text{CH}_3)_2-\text{NR}_2]^+$	-(CH ₂) ₉ CH ₃
Dodecyltrimethylammonium	DDTMA ⁺	$[(\text{CH}_3)_3-\text{NR}]^+$	-(CH ₂) ₁₁ CH ₃

Table 2. Common examples of organic exchange cations.

3.4.1 Surface Adsorptive Organoclays.

The first workers found that alcohols⁹⁸, dihydric alcohols⁹⁹, glycols¹⁰⁰ and nitriles¹⁰¹ were all adsorbed by montmorillonite. In 1949 Jordan⁸ found that the hydrophilic properties of the clay could be decreased by exchanging the inorganic cations of montmorillonite with large organic ammonium ions. The amine clay derivatives would then, when immersed in a dilute aqueous solution of phenols, show preferential adsorption of the organic material. It was then considered that if silicates were

exchanged with ions large enough to hold the layers apart, but without filling the interlamellar space, then a range of shape selective microporous sorbents could be obtained. This microporosity was first demonstrated in 1955 by Barrer and MacLeod⁹ who prepared TMA- and also tetraethylammonium- (TEA^+) exchanged montmorillonites. They found that in contrast to natural montmorillonites, polar organic species, paraffins and aromatic hydrocarbons were freely sorbed between the montmorillonite lamellae from the gaseous phase and the sorptive capacity was very much increased. At the same time Greene-Kelly^{102,103} was conducting x-ray diffraction studies to determine the orientation of adsorbed aromatic compounds on montmorillonite. He found that two orientations were common. The first, which is generally stable at low surface concentrations, has the plane of the aromatic ring parallel to the silicate sheet. At higher surface concentrations however, he found that the molecules re-orientate so that their planes are perpendicular to the silicate sheet.

Barrer and his co-workers then extended their studies to encompass a range of alkylammonium exchanged montmorillonites to characterise them as sorbents and to investigate their use for the separation of molecular species by selective intercalation^{104,105,106}. They demonstrated permanent intracrystalline porosity when the quaternary ammonium ions were replaced with mono-, di-, and trimethylammonium ions. The d_{001} spacings for the clay complex and the free distances, Δ ($d_{001}/\text{complex} - d_{001}\text{clay}$), are given in Table 3¹⁰⁴.

It can be seen that Δ is smaller than the van der Waals radius of the ions. This is attributed partly to compression of molecules between the sheets, but also to keying of the molecules into the hexagonal cavities in the tetrahedral sheet (Figure 2c).

Clay Derivative	$d_{001}/\text{\AA}$	$\Delta/\text{\AA}$	Radius of ion/ \AA
$(\text{CH}_3)_4\text{N}^+$	13.5	4.1	4.9
$(\text{CH}_3)_3 \text{NH}^+$	13.0	3.6	3.9
$(\text{CH}_3)_2 \text{NH}_2^+$	12.2	2.8	3.4
CH_3NH_3^+	12.0	2.6	3.25

Table 3. The d_{001} spacings for the clay derivative, the free distances Δ (d_{001} /complex- d_{001} clay), and the radius of the ion.

Barrer *et al.*¹⁰⁷ also found that the affinity of organic species for TMA-montmorillonite decreased in the order benzene > n-heptane > cyclohexane > iso-octane. Attempts to obtain a random distribution of sodium and alkylammonium cations within the clay layer, in order to control the sorptive capacity of the clay complex, were unsuccessful. Subsequent work suggests that cations segregate complete interlayers.

Although much of the earlier work had concentrated on adsorption from the gaseous phase, Cowan and White investigated a series of amine and Ethomeen (tertiary amine) exchanged montmorillonites for their capacity to absorb mono- and dihydric phenols from dilute aqueous solutions^{108,109}. They found that of the series ethylammonium to octadecylammonium-montmorillonite, dodecylammonium-montmorillonite was the most active. They proposed that condensation of adsorbate molecules on the organoclay surface occurs through electrostatic/hydrogen bond interactions at the hydrophilic sites and van der Waals forces at the organophilic sites.

In 1968, Slabaugh & Carter¹¹⁰ reported adsorption of 31 mg methanol/g dodecylammonium-montmorillonite. Stul *et al.*¹¹¹ were able to adsorb 9 to 330 mg

hexanol and 40 to 530 mg octanol/g dodecylammonium-montmorillonite in studies conducted over a wide range of alcohol concentrations. These observations for dodecylammonium-montmorillonite and studies by Weiss¹¹² suggest that dodecylammonium ions and dodecyldiammonium ions form pillars when adsorbed in the interlamellar space of montmorillonite.

In 1985, twenty years after the pioneering work of Cowan & White, Wolfe *et al.*^{113,114} looked at the adsorption of eleven organic pollutants (0.01 to 100%) on propyl-, dodecyl- and dodecyldiammonium-bentonites. The amount of phenol adsorbed on dodecylammonium-montmorillonite was very low but agreed with that found by Cowan and White^{108,109} which indicated that between 0.007 to 0.147 mg/g of phenol was adsorbed at equilibrium concentrations of 300 mg/L and 3200 mg/L, respectively. Wolfe *et al.*^{113,114} also found that propylammonium-montmorillonite performed best at low organic concentrations but dodecylammonium-montmorillonite was better at higher concentrations.

The cationic nature of primary amines, such as those used by Wolfe *et al.*^{113,114}, and hence their adsorption as cations on clay, is a function of pH. In contrast, the cationic nature of quaternary ammonium ions is independent of pH and so they are retained on the exchange sites by coulombic forces regardless of pH.

The late 1970s bought renewed interest in the work started by Barrer and his co-workers concerning tetraalkylammonium exchange cations. It was known that the large internal surface area created by some tetraalkylammonium ions greatly increased the available area for adsorption of organic molecules. It was hoped that this would lead to materials

that would be of use in removing small amounts of aromatic pollutants from natural water systems. Toxic and hazardous wastes are disposed of in many ways, but organic compounds can be released, leading to contamination of ground water, soil and air¹¹⁵.

In 1977, McBride *et al.*¹¹⁶ renewed interest in the adsorption of organics from aqueous solution when they investigated the potential of Cu²⁺, TMA⁺, TEA⁺ and TPA⁺ exchanged montmorillonites as sorbents for benzene and phenol. They were able to adsorb 72 mg benzene/g TMA-montmorillonite.

Boyd and his co-workers have characterised the sorption of non-ionic organic contaminants (NOCs), such as aromatic and chlorinated hydrocarbons, as vapours and aqueous solutes by TMA⁺ and TMPA⁺ exchanged smectites^{117,118}. They found that the size of the organic cation, the hydration state of the system and the layer charge affected the surface area and pore structure of the organoclays and hence their adsorption efficiencies.

- Lee *et al.*⁸³ found that the adsorption of benzene, toluene and xylene vapours by the TMA-smectite was greater than their adsorption as solutes from water. The lower adsorption efficiency of TMA-smectite in presence of bulk water was described as a water induced sieving effect and attributed to shrinkage of the interlayer pore sizes by hydration of TMA⁺ cations and/or aluminosilicate surfaces of the clay layers. This study also demonstrated shape selectivity by TMA-smectite as evidenced by a progressive reduction in uptake in going from benzene to the larger aromatic compounds. However, this progression was only noted for uptake from solution, not as vapours. This property was attributed to shrinkage by water of the interlamellar

cavities in which adsorption of the aromatic molecules occurred. In addition, the isotherms for sorption of aromatic compounds from water were not linear. Also, the more water soluble benzene showed considerably greater affinities for the TMA-smectite than the less soluble trichlorobenzene¹¹⁸.

- Lee *et al.*¹¹⁹ and Jaynes and Boyd¹²⁰ also observed that benzene, toluene and xylene were adsorbed from water by TMA⁺ exchanged clays but also that the adsorption of these aromatics was more pronounced on clays with a low charge density in which the prop-like tetramethylammonium ions were further apart.
- Even though the surfactant treated clays have a much higher carbon content, TMA⁺ and TMPA⁺ exchanged clays sorbed more benzene, toluene and xylene⁸⁴. Furthermore, the amount sorbed increased as the amount of available siloxane surface increased, thus supporting the view that the siloxane surface was hydrophobic. The aromatics were considered to be adsorbed onto the exposed siloxane surface.
- Jaynes and Boyd¹²⁰, persevered in this vein and studied the adsorption of a range of alkylaromatics from water onto TMPA⁺ exchanged clays, in which the charge density on selected clays was reduced using the Hofman-Klemen effect (Section 2.4). This approach led to a reduced number of interlayer TMPA⁺ ions and resulted in a change from partition into the organic phase to adsorption onto the more exposed siloxane surface. These results are extremely significant because the change from partition to adsorption reflects a specific interaction between the adsorbate and the adsorbent which may be fine-tuned or used to extract one adsorbate in the presence of others. Jaynes and Boyd¹²⁰ again concluded that sorption occurred primarily on the

aluminosilicate surfaces. Furthermore, unlike TMA-smectite, adsorption efficiencies of TMPA-smectite from bulk water were not strongly affected by adsorbate size and shape.

- The tetramethylphosphonium cation (TMP^+) is a group VA analogue of the TMA^+ cation and is thus expected to be less strongly hydrated than the TMA^+ cation, which has an appreciable hydration energy of 32 kcal/mole¹²¹. This enabled a detailed study of the effect of cation hydration on the adsorption efficiency of organoclays¹¹⁸. The adsorption of organic vapours by TMA-smectite was not strongly dependant on the size and shape of the adsorbate, whereas the extent of adsorption from water was significantly reduced as the size and shape of the adsorbate grew larger and bulkier.

The behaviour of organophilic clays will now be discussed in more detail.

3.4.2 Organophilic Clays.

During the 1980s research concentrated on the treatment of soils with QACs with large alkyl chains. It was known that low organic matter soils, clays and aquifer materials had little sorptive capacity for the removal of NOCs from water and were therefore ineffective in attenuating organic contaminant mobility^{93,94}. Increasing the organic matter however, could be achieved by simple exchange of the naturally occurring inorganic cations with large organic cations. The solubility enhancement of NOCs by large QACs, which reduces the transport potential of otherwise mobile species, suggested a potentially important tool in chemical and biological remediation of contaminated soils and sediments. However, most environmental remediation efforts

involve soil-water or sediment-water systems where both NOC and organic cations may interact with the solid phase. There was therefore a need to understand the effects of the organic cations on the distribution of NOCs in soil-water systems. Understanding the whole system is a massive area of research and this thesis is restricted to investigating the interaction of organic cations with clay minerals - a significant component of soil systems.

When large organic cations are fixed on the clay surface, an organic phase forms that is derived from the alkyl hydrocarbon chain. This organic phase functions as a partition medium for NOCs and is highly effective in removing such compounds from water¹²².

In recent years Boyd and his co-workers have carried out much of the research into alkylammonium-smectites as sorbents. Their work with surface adsorptive clays has been discussed above. Their interest in soil treatment has driven studies of long chain alkylammonium exchange as a method of increasing the organic carbon content of soils¹²³.

Boyd and his co-workers investigated the sorption characteristics of various NOCs and ionisable organic compounds (IOCs), including benzene, trichloroethylene (TCE)¹²⁴, phenol and chlorophenols^{117,125} by organoclays from both aqueous solution and the vapour phase. They compared organophilic clays (i.e. organoclays prepared using organic cations that are very hydrophobic in nature e.g. dioctadecyldimethylammonium (DODMA⁺) and hexadecyltrimethylammonium (HDTMA⁺)), and surface adsorptive organoclays (i.e. those having minimal hydrophobic properties such as TMA⁺)^{96,126,127}. They showed that in general:

- The sorptive capacity of the modified clays was greatly increased, compared to that of the unmodified clays.
- Dry organophilic clays acted as dual sorbents whereby the ‘free’ aluminosilicate mineral surface functioned as a solid adsorbent, and the bulky organic moieties of the exchange ions functioned as a partition medium, analogous to the behaviour of natural dry soil¹²⁸.
- In aqueous solution, adsorption on the free mineral surfaces was minimised by the strong competitive adsorption of water and uptake of NOCs by organophilic clays was due mainly to solute partitioning into the organic medium formed by the alkyl groups of the exchange ions. The theory of a partition mechanism is supported by (i) highly linear adsorption isotherms, (ii) dependence of the sorption coefficient on the water solubility of the NOC, and (iii) dependence of the sorption by the organoclays on the organic carbon content of the modified clay.
- The uptake of organic vapours by dry organophilic clays was greater than that by water saturated organophilic clays because of concurrent adsorption on mineral surfaces and consequently, vapour uptake isotherms were non-linear.
- It was also found that phenol and its chlorinated congeners were sorbed by the organophilic clays in proportion to the number of chlorine atoms on the phenol structure. Thus, phenol itself was not sorbed significantly by these organoclays but trichlorophenol was strongly sorbed, i.e. as the hydrophobicity of the molecule increased, sorption of chlorophenols from water increased.

- For the very hydrophobic clays the uptake of, for example pentachlorophenol (PCP), was via non-polar interactions between the alkyl (e.g. -C₁₈) groups on the organic cation and PCP, i.e. a partitioning process. The organic phases of organophilic clays (e.g. DODMA-smectite) were about 10 times more effective than the organic matter of natural sediments for removing PCP from water. The surface adsorptive organoclays with their separate small organic moieties, did not give rise to phases which acted as an effective partitioning medium despite a significant carbon content, hence very little PCP was taken up.
- In studies of soils exchanged with organic cations, HDTMA⁺ proved more effective than dodecyltrimethylammonium (DDTMA⁺) and nonyltrimethylammonium (NTMA⁺) for the adsorption of nonionic organic contaminants from water¹¹. Indeed HDTMA⁺ treated soil was 10 to 30 times more effective than natural soil organic matter in the uptake of benzene, dichlorobenzene and TCE from water¹²⁹.
- In contrast, it was found that surface adsorptive organoclays showed very weak sorptive capabilities for the phenolic compounds tested, although the amount of sorbed benzene, toluene and xylene, was in general, considerably greater on TMA-clays than for HDTMA-clays despite the latter having a much greater organic carbon content. Also, adsorption isotherms tend to be non-linear for surface adsorptive organoclays and this has been discussed above (Section 3.4.1).

3.5 INFLUENCE OF EXCHANGEABLE CATIONS.

Patzko *et al.*¹³⁰ studied the influence of the resident inorganic cation on the uptake of hexadecylpyridinium (HDPY^+). They observed that the maximum uptake increased in the order $\text{Ca}^{2+} < \text{K}^+ < \text{Mg}^{2+} < \text{Na}^+$ for addition of HDPY^+ to the different cation exchanged clays which reflects the swelling ability of the clays (as discussed in Section 2.5).

3.6 SORPTION OF DIFFERENT CLASSES OF CONTAMINANTS.

Stapleton *et al.*¹³¹ studied the sorption of pentachlorophenol to HDTMA-clay as a function of ionic strength and pH. IOCs in the aqueous phase can exist either as a protonated or a deprotonated species. Sorption of the deprotonated species was represented by a Langmuir type isotherm and the sorption of the protonated species by a linear isotherm. They found that between pH 4.0 and pH 8.5 (the experimental pH range), the sorption decreased by three times and the aqueous solubility increased by three orders of magnitude as the dominant aqueous species changed from the protonated to the deprotonated form.

Sánchez-Camazano and Sánchez-Martín¹³² studied the adsorption from solution of two highly toxic organophosphorous pesticides, azinphosphomethyl (sparingly soluble in water) and dichlorvos (moderately soluble in water) by HDTMA-montmorillonite, DDTMA-montmorillonite and TMA-montmorillonite. They compared uptake on the organoclays with (i) that on natural montmorillonite, (ii) soil organic matter and (iii) the octanol-water partition coefficient (K_{ow}) of the compounds. They found that organic phases derived HDTMA^+ and DDTMA^+ were similar and significantly more effective for

the removal of azinphosphomethyl from water, than the soil (10-20 times more effective), and octanol (20-50 times more effective). However, these organic phases and the organic matter from the soil were equally effective at removing dichlorvos from water. Their efficiency was 50 times greater than that of octanol. TMA-montmorillonite was actually less effective than natural montmorillonite for both pesticides.

The interaction of radioisotopes with soils and minerals has been extensively studied because of the common practice of disposing of radioactive waste in landfill sites. For example, caesium^{133,134,135} and strontium¹³⁶ have been studied since caesium-135 (and to a lesser extent caesium-137) and strontium-90 are major constituents of the waste water effluents from nuclear reprocessing units¹³⁷. Isotopes of uranium and thorium have been investigated because of their natural occurrence as well as their presence in nuclear wastes^{138,139}. Clay minerals in general, exhibit extreme sorption capacity for such cationic fission products and actinides. However, they show only a weak interaction with radio-iodine which exists primarily as an anion in aqueous environments¹⁴⁰. However, organoclays such as HDTMA⁺, and HDPY-bentonite have been investigated as potential sorbents. Out of the alkylammonium ions tested, HD PY⁺ has proven to be the most effective in bringing about increased iodide sorption, most probably due to its aromatic character^{141,142}.

3.7 ALKYLDIAMMONIUM CLAYS.

Smith and Jaffe¹⁴³ compared sorption of tetrachloromethane from water by an alkylammonium clay (DTMA-montmorillonite) with sorption by an alkyldiammonium clay (DTMDA-montmorillonite) at 10, 20 and 35°C. Tetrachloromethane sorption of

DTMA-clay, where only one end of the 10 carbon alkyl chain of the DTMA⁺ cation is attached to the silica surface of the clay mineral, was characterised by isotherm linearity, non-competitive sorption, weak solute uptake, and a relatively low heat of sorption. In comparison, both ends of the 10-carbon chain of the DTMDA⁺ cation are attached to the silica surface, and tetrachloromethane sorption was characterised by non-linear isotherms, competitive sorption, strong solute uptake and a relatively high, exothermic heat of sorption that varied as a function of the mass of tetrachloromethane sorbed. Smith and Jaffe¹⁴³ concluded that the attachment of both ends of the alkyl chain to the interlamellar mineral surface appeared to change the sorption mechanism from a partition dominated process to an adsorption dominated process.

3.8 EXAMPLES OF APPLICATIONS.

3.8.1 Personal Monitoring Devices.

Harper and Purnell studied the adsorption of organic vapours on TMA⁺, TEA⁺, tert-octylammonium and myristyltrimethylammonium exchanged montmorillonites with a view to creating an adsorbent for use in vapour phase sampling systems for personal monitoring devices¹⁵. They found that TMA-montmorillonite showed the most promise.

3.8.2 In-Situ Modification of Sites.

Burris and Antworth¹⁴ have applied the observations of others and have studied the in-situ modification of an aquifer material by HDTMA⁺ to enhance retardation of organic contaminants, such as perchloroethylene (PCE) and naphthalene. Sorption isotherms on HDTMA-modified aquifer material were linear, and sorption coefficients were

increased by over two orders of magnitude relative to the unmodified material. Their results suggested that it is feasible to create a sorbent zone within an aquifer by injection of an aqueous solution of cationic surfactants. They suggested two possible ways that the sorbent zone would be useful. (1) Retardation within the sorbent zone allows time for slow degradation reactions to occur. (2) The sorbent zone would concentrate the containment mass within a significantly smaller area, making the engineering of environments suitable for degradation reactions more feasible. One problem with the use of surfactants in such practical applications is the associated foaming problem in handling. This could be overcome by the use of polymers as the organic exchange cation and is therefore of primary interest in this thesis.

3.9 SUMMARY OF GENERAL INTERACTIONS.

Clay minerals are electrically charged, have large surface areas and have the ability to adsorb organic molecules. Many polar organic molecules (e.g. alcohols, amines, ketones) are adsorbed onto the external clay surface, interlayer space and also on particle edges by electrostatic attraction and ion-exchange reactions. Adsorption of non-polar organic molecules (e.g. alkanes, aromatic hydrocarbons) by clay occurs by much weaker van der Waals attraction and is restricted to the external clay surface. Interactions by van der Waals attraction become progressively more significant as the molecular weight of the organic cation increases¹⁴⁴.

When organic compounds are adsorbed by clay from aqueous solution, the adsorption products normally retain both the organic compound and water in the interlamellar region. The interlamellar water is important in controlling the adsorption of large

uncharged organic molecules from aqueous solution^{90,145} since the desorption of water from the clay surface when organic molecules are adsorbed normally gives rise to a favourable entropy contribution to the free energy of adsorption¹⁴⁶.

3.9.1 Adsorption of Organic Cations.

The key points can be summarised as follows:

- The Gibbs free energy change for the exchange of inorganic cations by alkylammonium cations on montmorillonite increases linearly with the molecular weight of the organic cations^{147,148}. Small alkylammonium compounds are only adsorbed by cation exchange mechanisms¹⁴⁹ and give rise to the surface adsorptive clays, whereas QACs with chain lengths greater than a critical value ($>C_{10}$) are adsorbed via both cation exchange and hydrophobic bonding¹⁵⁰.
- In addition to the QAC size, the composition of electrolyte solutions may also affect the chemical stability of QAC-clay complexes by influencing the degree of QAC adsorption via hydrophobic bonding. Previous studies with soils have demonstrated that higher ionic strength resulted in increased QAC adsorption by hydrophobic bonding¹²⁷.
- Changing the companion anion from Cl^- to Br^- or SO_4^{2-} also increased QAC adsorption via hydrophobic bonding¹²⁶.
- Finally, clay type also affects organic cation adsorption by determining the arrangement of adsorbed organic cations in the clay interlayers and on the clay

3.9.2 Adsorption of Pollutants from Solution.

The key points can be summarised as follows:

- Sorption of nonionic organic compounds to clay modified by the exchange of monovalent quaternary ammonium cations having only small or rigid functional groups (e.g. methyl-, ethyl- or benzyl-) is characterised by relatively strong solute uptake, isotherm non-linearity, and competitive sorption. In addition the magnitude of solute uptake is not strictly dependant on the solutes aqueous solubility. This behaviour is caused by surface adsorption.
- In contrast, sorption of nonionic compounds to clay modified with monovalent quaternary ammonium cations having one or more large alkyl functional groups (e.g. 11 - 18 carbon alkyl chains) is characterised by relatively weak solute uptake, isotherm linearity and non-competitive sorption in which the magnitude of solute uptake is inversely proportional to the solute's aqueous solubility. This behaviour is caused by a partition process.
- Depending on the molecular structure of the organic cation, the modified interlamellar space functions as an adsorbent or a partition medium for the uptake of nonionic organic solutes.

3.9.3 Mechanisms of Interaction.

Small QACs are considered to exist as discrete species on the clay surface, and do not form an organic partition phase (Figure 10). Surfactant aggregation on silicate surfaces is considered to occur above a critical concentration called the hemimicellar concentration (HMC) subsequent to which adsorption proceeds by formation of further aggregates of a similar size and then forming even bigger aggregates¹⁵². This continues until mono- or bilayer surface coverage is complete or the critical micellar concentration (CMC) is reached thus forming a supported organic phase into which partition can occur. A consequence of this adsorption process is the change in the zeta potential of the solid-liquid interface which reverts from negative to positive values (Figure 6).

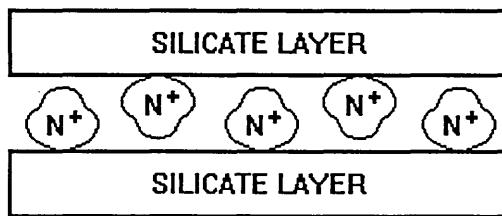


Figure 10. Showing the arrangement of TMA⁺ cations on the clay surface.

Relationships between layer charge and the interlayer expansion of clay minerals by larger alkylammonium cations were determined by Lagaly and Weiss¹⁵³ and Lagaly¹⁵⁴. Depending on the length of the alkyl chain and the mineral charge, the alkyl chains of the cations may form either monolayers, bilayers, pseudotrimolecular layers or paraffin complexes (Figure 11). A small organic cation such as hexylammonium forms monolayers in smectites but must form bilayers to neutralise the greater charge in vermiculites. Similarly with a larger organic cation, bilayers form in smectites but paraffin complexes form in vermiculites.

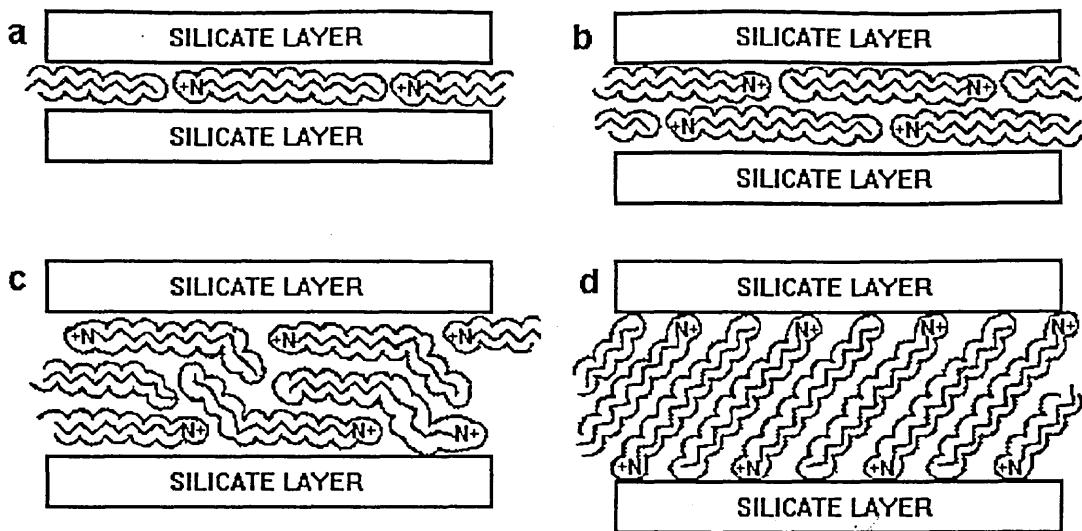


Figure 11. Showing the alkylammonium expansion of clay minerals (after Lagaly and Weiss¹⁵³ and Lagaly¹⁵⁴): (a) monolayer (13.7 Å), (b) bilayer (17.7 Å), (c) pseudotrimolecular layer (21.7 Å), (d) paraffin complex (> 22 Å).

Intercalation of organic cations causes a significant swelling of the clays and consequently an increase in interlamellar separation. This spacing changes as the size of the interlayer cations increases in such a way that one observes stepwise increases in the basal spacing of the clays due to the transition from monolayer to bilayer and from bilayer to pseudotrimolecular^{155,156,157,158}. Hence, the basal spacing of a clay will give an indication of which complex is present.

For a heterionic smectite with a basal spacing of 9.4 Å, exchange with TMA⁺ or TMPA⁺ will increase the basal spacings to 14.0 and 15.2 Å respectively. This agrees with the size of a TMA⁺ ion which is 4.9 Å and also suggests some keying of a methyl group into the aluminosilicate sheets⁸⁴. This agrees with the findings of Barrer and his co-workers as discussed in Section 3.4.1^{104,105,106}. The data also indicate that the triangular bases of the TMA⁺ and TMPA⁺ ions are parallel to the clay sheets and are likely to adhere alternatively to the upper and lower clay layers. A spacing of 15.2 Å

also allows for the aromatic ring of the TMPA^+ cation being perpendicular to the aluminosilicate sheets.

In the case of the longer, monosubstituted alkyl chains, the interlamellar space varies from 13.7 Å when the carbon number (n_c) < 13 up to 17.7 Å for $14 < n_c < 18$. If $n_c < 13$, the alkyl chains will form a monolayer and if $14 < n_c < 18$, the chains will form a bilayer¹⁵⁹. For $n_c > 18$ a pseudotrimolecular structure is proposed to explain the 21.7 Å distance^{154,160} (Figure 11).

The interlayer distances are affected by nature of the bonding. Xu and Boyd^{126,127} found that HDTMA^+ was initially adsorbed by cation exchange in the interlayer, causing extensive clay aggregation. As the loading increased, HDTMA^+ adsorbed to the external surfaces of aggregates via both cation exchange and hydrophobic bonding, the latter causing positive charge development on surfaces leading to redispersion of the clay particles. When the equilibrium concentration of HDTMA^+ reached the CMC, no further HDTMA^+ adsorption occurred. Desorption of HDTMA^+ was more significant when the HDTMA^+ retention mechanism was hydrophobic bonding. In addition it was found that highly dispersed clays (e.g. Na-montmorillonite in dilute NaCl solutions) lead to a random HDTMA^+ distribution on the surfaces, larger distances between silicate layers, and hence reduced lateral interactions between alkyl chains of adsorbed HDTMA^+ . Accordingly, cation selectivity coefficients were low at low HDTMA^+ loadings and increased dramatically as HDTMA^+ loading increased, resulting in a unique S-shaped adsorption isotherm. Initially flocculated clays (e.g. Na-montmorillonite in concentrated NaCl solutions) lead to HDTMA^+ segregation and more compact adsorption layers, which enhanced the lateral interactions between alkyl groups. As a result the cation

selectivity coefficients were high even at low HDTMA⁺ loadings and changed little as loading increased. Both cation exchange and hydrophobic bonding were involved in HDTMA⁺ adsorption at high loadings (e.g. > 0.75 CEC). Hence, charge density of clays, ionic strength of the bulk solution and the type of companion anions all affect the extent to which hydrophobic bonding contributes to the adsorption of HDTMA⁺.

These factors must be considered for industrial applications. For example, in the application of in-situ soil modification, quaternary ammonium cationic surfactants are likely to be introduced into the subsurface via injection wells resulting in a surfactant concentration gradient moving away from the point of injection and uneven HDTMA⁺ loadings across the soil profile. In some regions (e.g. the wetting front) the surfactant loading would be less than the CEC of the soil and the surfactant molecules will be adsorbed at ion-exchange sites. In other regions the amount of the surfactant may exceed the CEC resulting in a portion of the surfactant being adsorbed by hydrophobic interactions¹⁵¹. Extensive hydrophobic bonding of surfactant molecules could cause a build-up of positive charge on the clay surfaces leading to disaggregation of the organoclays, mobilisation of the dispersed particles, and undesirable changes in the hydraulic properties of the treated zone. Furthermore, HDTMA⁺ adsorbed to clay is essentially non-toxic to pollutant-degrading bacteria in soils whereas aqueous-phase HDTMA⁺ exerts considerable toxicity¹⁶¹.

3.10 CLAY-POLYMER INTERACTIONS.

3.10.1 Introduction.

Polymers have long been used to control the stability of solid/liquid dispersions. Generally it has been found that adsorbed polymer layers can, depending on the conditions either keep particles apart (deflocculate) or bind them together (flocculate). The oldest examples known are (i) for stabilisation, the Egyptian process for manufacturing ink with carbon black particles stabilised in water by natural gums, and (ii) for separation, the clarification of muddy streams by polymers released from some naturally occurring algae. In more recent times there has been a great interest in polymers as soil conditioners, i.e. adhesives which can agglomerate soil particles in order to give a better structure to the soil. Polysaccharides and carbohydrates were used as the first soil conditioners in the 1940s^{162,163}. Polymers used as soil conditioners have to become insoluble in the soil otherwise the water stability of the agglomerated soil particles is poor. Insolubilization can be achieved by adsorption of the polymer on clay present in the soil; insoluble complexes are formed which maintain adhesive properties. Hence, adsorption of water soluble polymers on clays is of vital importance for soil conditioning.

Processes in clay and soil systems essentially occur in an aqueous environment so the role of water must be considered. Hence, water soluble polymers have been extensively studied as complex formers with clays. As discussed previously in this chapter, water will compete strongly for adsorption sites on the clay surface, particularly where hydrogen bonding can occur. Being bifunctional however, water can act as both a hydrogen bond donor and acceptor so that its presence at the adsorbent surface may

either promote or inhibit polymer adsorption. Water molecules at clay surfaces are associated more with the exchangeable cations than with the silicate surface since the basal oxygens are weak electron donors (Chapter 2) and so hydrogen bonds are weak.

A common feature of both aqueous and non-aqueous systems is that a large number of solvent molecules must be desorbed in order to accommodate a single polymer molecule. The entropy gained provides the driving force for polymer adsorption, although electrostatic forces are also involved with cationic polymers.

To date, polycation adsorption on clays has mainly been studied in relation to soil conditioning and flocculation in water treatment plants¹² and their propensity as selective sorbents for organic pollutants has not been considered. Adsorption of polycations on clays can change the surface properties of the clay from hydrophilic to organophilic in a similar way to the organic cations discussed above. In principle these polycations offer considerable opportunities for fine tuning of selective adsorption properties. A significant advantage of the polycation is that the regularly spaced cationic groups may ensure a more even distribution of organic over the available surface in contrast to the more common surfactant molecules which associate in hemimicelles¹⁵² on the clay surface, thus forming a supported organic phase into which the pollutants undergo partition. Controlling the length of the spacer group between the cationic centres on the polymer will effect the amount of surface covered by the polymer, and thus the amount of available hydrophilic surface, and the organic carbon content of the clay. Patches of adsorbed polycation may also be found which leave free space on the aluminosilicate surface.

A further processing advantage exists so far as the polycations are produced as highly concentrated aqueous solutions (40% by weight of polymer). Thus the potential manufacturer would be able to operate at economic, high solids contents without the problems of foaming associated with surfactant treatments.

3.10.2 Organic Polymers.

Organic polymers represent a class of macromolecules built up by repetition of small simple chemical (termed 'repeat') units. In some cases, the repetition is linear, much as a chain is built up from its links. In other cases the chains are branched or interconnected to form a three-dimensional network. The length of an organic polymer chain is specified as the number of repeat units, also identified as the degree of polymerisation (DP). The molecular weight of a polymer is the product of molecular weight of the repeat unit and DP. In addition to being multisegmented and possessing very high molecular weights, organic polymers have several functional groups that allow them to interact with clay surfaces¹⁶⁴.

The interaction of clays with simple organic compounds has been fairly well characterised with respect to the mode of bonding and the orientation adopted at the clay surface. To an extent the information gained can be related to the behaviour of polymeric compounds although there are some significant differences¹⁶⁵. These differences essentially arise from the fact that besides being long, a polymer chain is flexible, multisegmented and often polyfunctional, and hence:

- May adopt various conformations in solution and so become attached to the clay

surface by numerous segment-surface bonds, the number of possible conformations increasing with increasing chain length.

- The large number of potential bonding sites is greater and so gives rise to a large net energy of adsorption.
- Since there are numerous potential configurations, it is statistically unlikely that the polymer will adopt a configuration corresponding to the minimum free energy of the system, hence a metastable conformation will arise.
- The rate of desorption is very small in systems where solvent-surface interactions are weak, thus adsorption is regarded to be irreversible. It is also statistically unlikely that all of the adsorbed segments can be simultaneously detached from the surface and remain so long enough for the polymer to move away from the interface.
- Polymer systems generally take a longer time to reach equilibrium because of the greater size of the molecules, although this does depend upon the nature of the clay, the exchange cation and the polymer.

Accessibility, solubility, temperature and steric factors will also contribute to the interaction process, as does the order of mixing the components of a system. Thus, the complex field of clay-polymer chemistry is still largely a descriptive science, although there is great interest in the area because of the many industrial applications. Since such a wealth of information is available, this work must restrict itself to the most relevant.

Q will define the amount of polymer adsorbed by the clay, whereas Q_{\max} will represent the maximum adsorption value.

3.10.3.1 Nonionic Polymers.

The adsorption of nonionic polymers is essentially an ‘entropy driven’ process since numerous water molecules are desorbed from the clay surface as the polymer molecules are adsorbed¹⁶⁶. The interaction of the nonionic polymers with the surface is mainly through hydrogen bonds (e.g. between the hydroxyl functional group of the polymer and silicate oxygens of the clay surface) which results in a very small, or even positive enthalpy change; and through various dipole-dipole or charge-dipole interactions¹⁶⁷.

In solution the polymer tends to adopt the conformation of a random coil, rather than that of a stretched out chain. Upon adsorption onto the clay surface however, the polymer spreads out and adopts a conformation allowing maximum segment-surface contact. The result is generally a series of adsorbed polymer segments, known as ‘trains’, which are interspersed with three dimensional ‘loops’ which extend away from the surface, the chain terminating at each end with two free-moving ‘tails’. This property of nonionic polymers make them particularly suited to stabilising a particular structure, although their behaviour in solution makes them relatively poor flocculants.

It is generally accepted that nonionic polymers are irreversible adsorbed onto the surface of clays and consequently no rearrangement in polymer configuration can take place after adsorption. This is because the probability that all train segments of the polymer will be detached from the surface for sufficient time for the polymer chain to move away into the

bulk solution is very small¹⁶⁸. The net segment-surface interaction energy, ε , is only of the order of 1 kT unit, however the total energy of adsorption can be very large due to the large number of adsorbed segments. The fraction of train segments, p , which for nonionic polymers is approximately 0.4 (i.e. an average of 40% of the total number of segments may be in flat contact with the clay surface), is therefore an important parameter.

3.10.3.2 Influence of Molecular Weight.

In general, for deflocculated clay minerals the amount of polymer adsorbed increases with the size or molecular weight of the polymer if surface accessibility is not restricted. Bottero *et al.*¹⁶⁹ studied the adsorption of non-ionic polyacrylamide on Na-montmorillonite and found that as the molecular weight of the polymer increased from 4.4×10^4 to 3×10^6 , Q_{\max} increased from 190 to 680 mg/g respectively. They also found that for $Q \approx 200$ mg/g the polymers assumed a statistically flat conformation, but for higher Q values the polymers made larger and larger loops into the bulk solution.

Exceptions to Q increasing with increasing molecular weight arise in some condensed clay-water systems where molecules beyond a certain size are physically excluded from some pore surface. Schamp and Huylebroeck¹⁷⁰ investigated the adsorption on clay of neutral polyacrylamide (PA) with varying molecular weights and were able to distinguish between surface adsorption and interlamellar (pore) adsorption. They suggested that pore adsorption is slow as polymer molecules enter with difficulty, and indeed found that the slow pore adsorption by H-montmorillonite almost disappeared when the PA was sufficiently large to be completely restricted from the pore regions of the clay. They

also suggested that surface adsorption is fast and that adsorption increases with increasing molecular weight which is in agreement with Bottero *et al.*¹⁶⁹. Schamp and Huylebroeck¹⁷⁰ also noted a normal temperature dependence for an exothermic reaction, i.e. raising the temperature decreased the adsorption.

3.10.3.3 Influence of Exchangeable Cations and Ionic Strength.

Adsorption is also influenced by the valence of the exchangeable cation associated with the clay surface and the pore electrolyte concentration, mainly due to their effect on interlayer accessibility. (The effect of the exchangeable cation on interlayer distance has been discussed in Section 2.5). An increase in exchangeable cation valence or an increase in pore electrolyte concentration diminishes the amount of neutral polymer adsorbed by the clay surface. As the ionic strength increases, there is less scope for interlayer swelling or for the tactoids to move further apart and so the amount of surface accessible to the polymer is reduced. Greenland¹⁷¹ found that for the addition of polyvinylalcohol to montmorillonite, Q_{\max} decreased rapidly as increasing aliquots of NaNO₃ were added to the system. Changing the added salt concentration from zero to 1.0 mol/L caused Q_{\max} to decrease from 750 mg/g clay to 120 mg/g clay. This coincided with a decrease in basal spacing.

3.10.4 Charged Polymers.

The interactions with charged species are more complex, since polyelectrolytes may undergo changes in surface charge and conformation in response to changes in the pH and ionic strength of the ambient solution.

3.10.5 Anionic Polymers.

Unlike nonionic polymers (and cationic polymers as discussed below Section 3.10.6), anionic polymers do not enter the interlayer space of expanding layer silicates¹⁷². Anionic polymers tend to be repelled by the similarly charged clay surface and generally, little adsorption occurs in suspension. Uptake may be altered however, by altering certain condition of the system such as the exchangeable cations associated with the clay and the pH and/or ionic strength of the medium.

3.10.5.1 Influence of Exchangeable Cations.

Adsorption is promoted by the presence of multivalent cations on the clay surfaces which act as ‘bridges’ between anionic groups of the polymer and negatively charged sites on the clay. This was suggested by Mortensen¹⁷³ following his studies of hydrolysed polyacrylonitrile (HPAN) adsorption on kaolinite. He found that Q_{\max} increased for exchange cations in the order $\text{Na}^+ < \text{K}^+ < \text{NH}_4^+ < \text{H}^+ < \text{Ba}^{2+} < \text{Ca}^{2+} < \text{Th}^{4+}$. With the exception of H^+ this is also the order in which cations reduce the zeta potential of the clay, thus allowing the polyanions to approach the surface more closely and increasing the probability for polymer-surface bonding.

3.10.5.2 Influence of Molecular Weight.

As for the behaviour with nonionic polymers, it would be expected that an increase in polymer molecular weight would lead to an increase in Q values. Indeed this was supported by Stutzmann and Siffert¹⁷⁴ who studied the addition of partially hydrolysed polyacrylamide (PHPA) onto Na-montmorillonite. Increasing the molecular weight from 6×10^6 to 11×10^6 caused Q_{\max} to increase from 2.4 mg/g clay to only 2.8 mg/g clay,

which is a much less significant effect than for nonionic polymers. They suggested that sorption is also related to the $\text{CONH}_2\text{COO}^-$ ratio. This determines the length of the carbon chain and the molecular weight, both of which control the accessibility of the organic molecule to the clay surface. Stutzmann and Siffert¹⁷⁴ also confirmed that the anionic polymer is sorbed exclusively on the external surface of the clay with the organic molecules protonated on the surface and adsorbed by ionic forces. They observed two simultaneous types of sorption, (1) a strong irreversible sorption involving a monolayer of chemisorbed molecules, and (2) a more extensive but weaker sorption wherein molecules are retained by hydrogen bonding and are easily removed by gentle heating.

3.10.5.3 Influence of pH and Ionic Strength.

Appreciable uptake can occur under acid conditions ($\text{pH} < 7$) and/or at high pore electrolyte concentrations when the negative charge on the polymer is neutralised by protons from the acid medium and/or is screened by the high pore electrolyte concentration. Mortensen¹⁷³ observed the effect of charge screening for the addition of hydrolysed acrylonitrile (HPAN) to kaolinite when Q_{\max} increased from 1 mg/g clay to 8.5 mg/g clay when the pH was decreased from 9 to 3.

Under acid conditions anionic polymers may also adsorb on the broken edges of the clay by attraction between the negative groups of the polymer and the positive aluminium ions exposed at the broken edges¹⁷⁵. Lee *et al.*¹⁷⁶ studied the effect of pH on the addition of PHPA to kaolinite and noted that an increase in the solution pH resulted in a decrease in Q_{\max} . This was attributed both to the polymer becoming increasingly charged

due to dissociation of acrylic groups and also to the increased negative charge on the clay edge surface.

Espinasse and Siffert¹⁷⁷ studied the influence of ionic strength on polyanion uptake by studying the same system as Stutzmann and Siffert¹⁷⁴ described above (PHPA adsorption Section 3.10.5.2), but in the presence of 100 g/L NaCl. They confirmed that an increase in molecular weight slightly increased the Q values, but they found a five fold increase in Q_{max} values under high ionic strength conditions. As the molecular weight of PHPA increased from 6×10^6 and 11×10^6 , Q_{max} increased from 13 mg/g clay to 15 mg/g clay. They suggest that the increase in ionic strength (salinity) has the effect of screening the negative charges on the polymer both from one another and from those associated with the clay platelets. This therefore allows the polymer greater contact with the clay surface.

Ben-Hur *et al.*¹⁷⁸ also looked at anionic polyacrylamide adsorption and found that adsorption increased with the electrolyte concentration in agreement with Espinasse and Siffert¹⁷⁷. They concur that an increase in electrolyte concentration results in a compression of the electric diffuse double layer at the clay surface and enhances neutralisation of the charge of the anionic polymers.

3.10.6 Cationic Polymers.

When compared with nonionic and anionic polymers, cationic polymers have received relatively little attention. This may be due to the fact that soil organic matter or humus, which is associated with the clay fraction, largely consists of anionic polymers together

with small amounts of uncharged and amphoteric substances. Much of the information available on the polycation-solid interaction is concerned with their behaviour as aggregating agents rather than with their adsorption behaviour.

Adsorption of positively charged polymers by clays occurs largely through electrostatic (coulombic) interactions between the cationic groups of the polymer and the negatively charged sites at the mineral surface¹⁷⁹ leading to charge neutralisation. Here $\epsilon \gg 1$ kT unit (in the order of 4 kT¹⁸⁰) and $p > 0.7$ leading to almost complete collapse of the polymer chain on the surface¹⁶⁵. Indeed it is widely accepted that cationic polymers are irreversibly adsorbed onto the surface of clays and consequently no rearrangement in polymer configuration can take place after adsorption. Beyond a given level of polymer uptake a reversal of the clays negative surface charge can occur¹⁸¹.

Ueda and Harada¹⁸² investigated charge neutralisation and chain collapse by studying the adsorption of cationic polysulfone (diallyldimethylammonium chloride - SO₂ copolymer) of molecular weights 16.7×10^4 and 1.4×10^4 on Na-montmorillonite. They concluded that the adsorption of the polymer on the clay was irreversible since the polymer was not desorbed from the clay despite treatment with 3.0 M NaCl or CaCl₂. They also followed the changes in the CEC and the anion exchange capacity (AEC) of the complex as adsorption increased and found that as polymer adsorption increased so did the AEC, however the CEC decreased. The increase in AEC was attributed to the cationic groups contained in the loops and tails of the adsorbed polymer, and the decrease in CEC to charge neutralisation of the negative clay surface by train segments. They determined that p could be calculated from the difference in the amount of adsorbed polymer and the

AEC. They found that up to 50% coverage $p = 1$, and even at 100% coverage only about 25% of the segments were contained in loops and tails.

3.10.6.1 Influence of Exchangeable Cations.

Gu and Doner¹⁸³ investigated the adsorption of cationic polysaccharide (PSS) by illite saturated with difference cations at about neutral pH. They noted a H-type isotherm for Na-illite at equilibrium concentrations $< 140 \text{ g/m}^3$, indicating a very high affinity for the clay surface. At equilibrium concentrations $> 140 \text{ g/m}^3$, adsorption increased further and was attributed to multilayer adsorption. Q_{\max} for Na-illite was greater than for Ca-illite, with the latter exhibiting an L-type isotherm. Illite exchanged with hydroxy-Al polycations (Al-p, $10^4 < \text{molecular weight} < 5 \times 10^4$) resulted in a three-fold decrease in PSS adsorption compared with Na-illite. Na^+ resides mainly in the diffuse double layer and can be readily exchanged by other cations. Conversely, Al-p forms strong complexes with the clay surface and cannot be readily exchanged by other cations, especially monovalent cations¹⁸⁴. Excessive addition of Al-p can even reverse the surface charge on illite. Gu and Doner¹⁸³ suggested that the reduction of the active sites on the illite surface, due to surface complex formation, largely explained why the Na-illite adsorbed significantly more than the Al-p-illite. Also Ca^{2+} was not as effective as Al-p in forming a surface complex or in screening the surface negative charge and so Ca-illite adsorbed more cationic PSS than Al-p-illite. Al-p formed strong complexes with the clay surface and Al-p-illite formed large tactoids thus reducing accessibility of PSS to the clay surface. The order of PSS adsorption, Na-illite $>$ Ca-illite $>$ Al-p-illite, was related to tactoid size, Na-illite $<$ Ca-illite $<$ Al-p-illite, showing that accessibility to the clay surface was also significant.

Recently Breen *et al.*¹⁸⁵ investigated the effectiveness of the polycations FL15 and FL17 of general formula $[\text{Me}_2\text{NCH}_2\text{CHOHCH}_2]^{n+}$, and Magnafloc 1697, $[(\text{CH}_2\text{CHCH}_2\text{N}(\text{Me})_2\text{CH}_2\text{CHCH}_2)_n]^{n+}$ (with $-\text{CHCH}_2\text{N}(\text{Me})_2\text{CH}_2\text{CH}-$ forming a 5 membered ring) at displacing Cs^+ ions from Texas bentonite compared to Na^+ , K^+ , TMA^+ , and paraquat²⁺ ($(\text{C}_5\text{H}_5\text{N}-\text{CH}_3)_2^{2+}$). ^{133}Cs solution-phase NMR was used as an in-situ probe to study the adsorption of the polycations and other ions. They found that FL15 (molecular weight 5000), FL17 (molecular weight 100,000) and Magnafloc 1697 (molecular weight 100,000), exhibited high affinity adsorption isotherm on all the cation-exchanged forms of the bentonite. In contrast the adsorption of TMA^+ , which as in this thesis represents the cationic portion of the polymers, was of lower affinity. Q_{\max} depended on the resident exchange cation as $\text{Na}^+ > \text{K}^+ > \text{Cs}^+$ and on the molecular weight of the polymer. The greater the molecular weight of the polymer, the greater the value of Q_{\max} , as found by other workers as discussed below in Section 3.10.6.2. Breen *et al.*¹⁸⁵ also found that Q_{\max} on the Na-clay approached twice the amount of polycation required to fulfil the CEC of the clay. If all the cation exchange sites on the clay surface were satisfied by cationic units on the polymer then saturation would occur at Q_{\max} values of 83 mg/g for FL17 and 103 mg/g for Magnafloc 1697. This value was exceeded by the FL polymers on all cation-exchanged forms, although, Q_{\max} for Magnafloc 1697 on Cs-WL was only 68% of that required to satisfy the exchange capacity. XRD data confirmed that the polycations resided between the clay lamellae, except at low loadings on the Cs^+ clay. The data suggested that the FL polycations were able to penetrate the interlayer more effectively than the bulkier Magnafloc 1697.

In the same study, Breen *et al.*¹⁸⁵ found, as the adsorption isotherms suggested, that the polycations were extremely effective at displacing the resident Cs^+ ions, although the FL

polymers were more effective than Magnafloc 1697. Paraquat²⁺ was nearly as effective whereas TMA⁺ ions were considerably less effective and Na⁺ and K⁺ ions were ineffective.

3.10.6.2 Influence of Molecular Weight and Cationicity.

Denoyel *et al.*¹⁸⁰ investigated the interaction of a copolymer of acrylamide and N,N,N,-trimethylaminoethyl chloride (PCMA) of different molecular weights with Na-montmorillonite. They found that as the molecular weight of the PCMA was increased from 2×10^4 to 2×10^6 , the number of polymer segments adsorbed in trains decreased from 0.54 to 0.13. They suggest that both steric hindrance and electrostatic repulsion prevent two parts of a chain crossing on the clay surface and that an increase in molecular weight will increase the size of the loops.

The same French group has carried out studies on the interaction of PCMA and suspensions of silica^{186,187,188}. Silica particles usually have a net negative surface charge and so are representative of clay surfaces in the nature of the interactions between polymers and the surface. If m , and n , are the number of AM and CMA units in the random copolymers, the cationicity, c , is expressed by the relation $c = n/(n+m)$. It has been found that for a fixed molecular weight, as c decreased, Q_{\max} increased. Also, at low c , (e.g. 1%), an increase in molecular weight led to an increase in Q_{\max} since the molecular weight per unit charge is much higher, hence much higher weight adsorption is required before the CEC is satisfied. However, at high c , Q_{\max} is not significantly increased. The difference in behaviour is related to the degree of cationicity which gives rise to two different adsorption mechanisms. At low c , (<5%), the major adsorption

mechanism is via interparticle bridges. Bridging is made possible due to adsorption of a large excess of nonionic amide groups which allow unadsorbed ammonium groups to be present in long loops and tails which extend into the bulk solution away from the surface. At high c , ($> 15\%$), charge neutralisation dominates and PCMA adopts an essentially flat conformation on the surface. At intermediate values it is suggested that the two mechanisms can occur simultaneously¹⁸⁷.

Durand-Piana *et al.*¹⁸⁹ investigated the interaction of the same copolymer (PCMA) with Na-montmorillonite and observed the same trends as those found using silica suspensions. They found at low c (1%), increasing the molecular weight of the polymer from 8×10^4 to 2×10^6 caused Q_{\max} to increase from 1750 mg/g clay to 2650 mg/g clay. Conversely at 100% cationicity, Q_{\max} reached a constant value (250 mg/g clay) for the addition of either molecular weight of polymer thus indicating that Q was not weight dependant at high c .

3.10.6.3 Influence of pH and Ionic Strength.

Gu and Doner¹⁸³ also studied the effects of pH and ionic strength on cationic PSS adsorption by Na-illite. The pH was adjusted by dilute HClO₄ or NaOH, whereas the ionic strength was adjusted using NaClO₄. Increasing the pH from 3 to 10 increased PSS uptake (from 88 mg/g clay to 114 mg/g clay), perhaps as a result of an increase in positive edge sites. Increasing the ionic strength from zero to 200 mol/m³ had no significant effect on PSS uptake, since adsorption is driven primarily by surface charge neutralisation.

Q usually increases with ionic strength for colloids and polymers of opposite charge since an increase in the salt concentration decreases the repulsions between the loops and tails of the polyelectrolyte¹⁹⁰. However, high ionic strength may also cause flocculation thus reducing the available surface.

Ueda and Harada¹⁸² investigated the effect of NaCl on the adsorption of a cationic polysulfone (molecular weight 16.7×10^4), on Na-montmorillonite. They found that as the quantity of NaCl in the dispersion medium increased, the adsorption of the copolymer increased and the AEC of the complex increased. They suggested that the polymer chain in an NaCl solution exists in a coiled configuration and retains this configuration when it is adsorbed onto the clay surface. Hence the cationic sites of the polymer cannot combine effectively with the anionic sites of the clay thus the amount of apparent adsorption of the copolymer increases.

Conversely, Ben-Hur *et al.*¹⁷⁸ found that increasing the ionic strength led to decreasing Q values. They studied the adsorption of a cationic polysaccharide and a cationic polyacrylamide on montmorillonite and illite in aqueous solution at two ionic strengths. The results support the theory that adsorption of the polymers occurs mainly on the external surfaces of clay tactoids. They found that the higher the electrolyte concentration the higher the rate of clay flocculation, and thus the fraction of surface area which was found inside the intra-aggregate cavities was less accessible. Also, the competition between the inorganic cations and the cationic polymers adsorption for sites on the negatively charged clays also increased with the electrolyte concentration.

3.11 SUMMARY OF CLAY-POLYMER INTERACTIONS.

It is now generally accepted that the order of adsorption for clay-polymer systems is cationic > nonionic > anionic, that adsorption occurs mainly on the external surfaces of the clay particles and that the structure of the floccules have a dominant effect on the polymer adsorption^{191,178}.

The important polymer characteristics that affect adsorption are molecular size, molecular conformation and electrostatic charge. In addition, the external surface area, structure, and pore size of clay tactoids and clay type affect adsorption of polymers. Electrolyte composition and concentration in solution also influence adsorption¹⁹². The higher the electrolyte concentration the higher the rate of clay flocculation, and the fraction of surface area which is found inside the intra-aggregate cavities is, hence, less accessible. The competition between native inorganic cations and cationic polymers for sites on negatively charged clays also increases with the electrolyte concentration. Since an increase in electrolyte concentration results in a compression of the diffuse double layer at the clay surface and enhances neutralisation of the charge on anionic polymers, the adsorption of anionic polymers increases with the electrolyte concentration, as opposed to the decrease in the adsorption of cationic and nonionic polymers as this concentration is increased.

3.11.1 Mechanisms of Clay-Polymer Interactions and Flocculation.

As a result of their size, polymers can bind strongly to clay surfaces, even when the free energy of adsorption for one monomer unit is quite small. Moreover, they cannot be completely confined next to the surface and a sizeable fraction of the adsorbed polymer

lies away from the surface in loops and tails. It is through these loops and tails that opposing surfaces will interact. The range of interaction is the overall thickness of the adsorbed layers. Repulsions will be generated if the surfaces are completely saturated with polymers and the suspension will then be stabilised against aggregation. If the surfaces are unsaturated they gain adsorption free energy by sharing some polymer strands and this bridging attraction may cause particles to aggregate, and the dispersion to flocculate¹⁹³.

Napper¹⁹⁴ proposed several ways in which added polymer can affect the stability of an idealised colloid suspension (Figure 12) and these mechanisms can be applied to the interactions of polymers with clays.

- When low concentrations of adsorbing polymer are added to a stable dispersion (Figure 12a) of colloidal particles, the dominant adsorption mechanism is that of bridging flocculation (Figure 12b).
- When the colloidal particles are fully coated with polymer (saturated coverage), the like charges cause the particles to repel one another. This is known as steric stabilisation (Figure 12c).
- If the sterically stabilising polymer layer is thin, van der Waals forces may be large enough to cause weak coagulation (Figure 12d) between the particles.
- Addition of non-adsorbing polymer to sterically stabilised particles may lead to

depletion flocculation (Figure 12e). Addition of a large concentration of non-adsorbing polymer may lead eventually to depletion stabilisation (Figure 12f).

- Addition of a second adsorbing polymer, at low concentrations, to a sterically stabilised dispersion may lead to bridging heteroflocculation (Figure 12g).

In addition to the formation of interparticle bridges, flocculation by ionic polymers can also be caused by neutralisation of the surface charge, and electrostatic attraction between electrically opposed sites (the electrostatic patch model).

The electrostatic patch model of flocculation was proposed by Gregory¹⁹⁵ following his investigation into the effect of cationic polymers on the colloidal stability of latex particles. When highly charged polymers of molecular weight 5×10^3 , 5×10^4 and 1×10^5 were added to suspensions of negatively charged latex particles, extensive flocculation occurred in each case. Particle bridging was discounted as the method of flocculation since the two larger polymers appeared to flocculate the system at the same rate. The higher weight polymer would be expected to flocculate the system at a faster rate if particle bridging occurred. Moreover, the smallest polymer promoted substantial flocculation despite its comparatively small size in relation to the latex particles. Such highly charged polymers would be expected, in theory, to adopt an essentially flat configuration on the surface. The consequent absence of a significant number of loops and tails means that interparticle bridging could not occur¹⁹⁶. Gregory also discounted charge neutralisation as the cause of the enhanced flocculation since a higher flocculation rate was observed for the addition of the polymers than for addition of NaNO_3 . In the

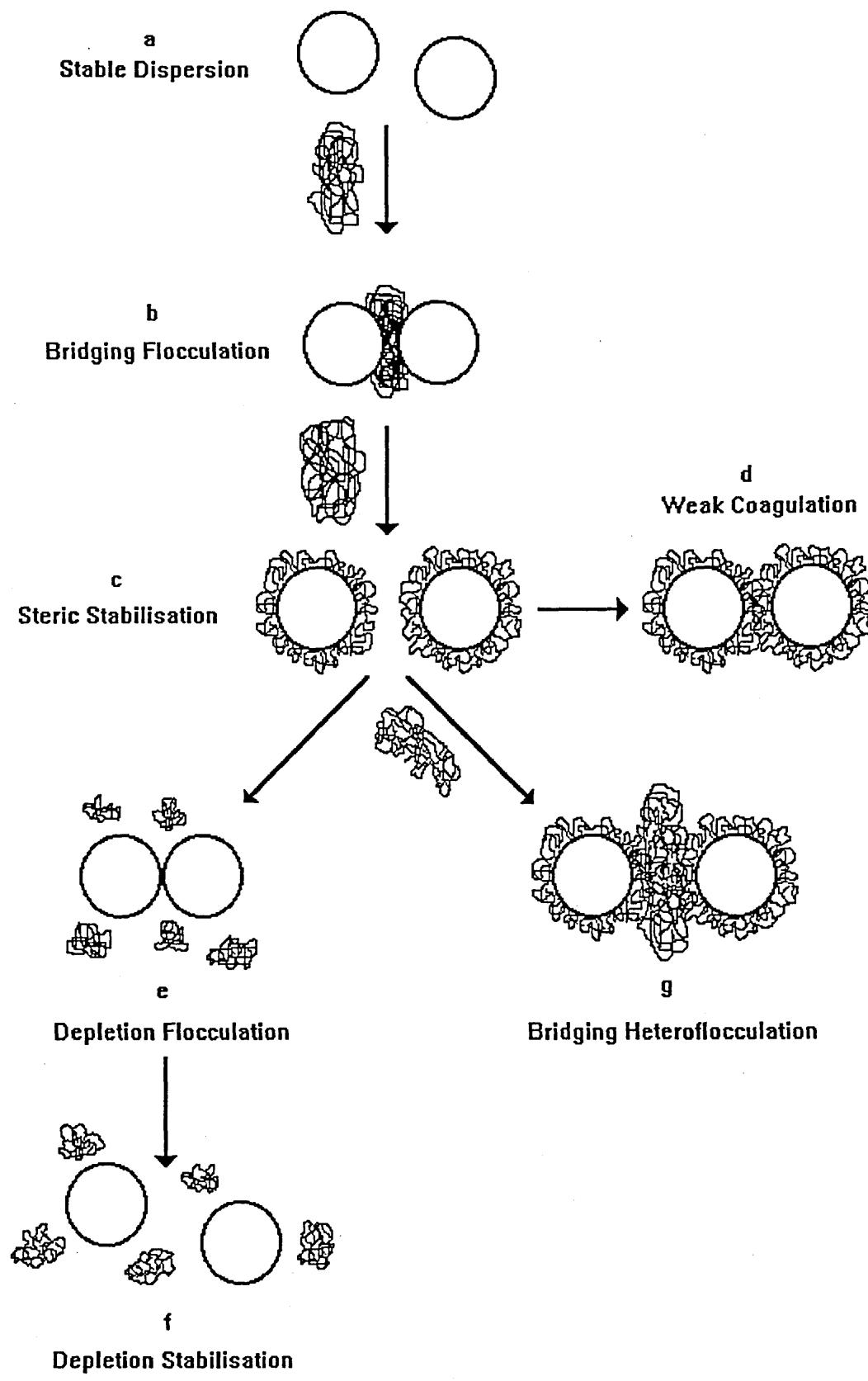


Figure 12. A schematic representation of the ways in which polymers can affect colloid stability (after Napper¹⁹⁴).

electrostatic patch model (Figure 13) the negative sites on the particle surface are not uniformly neutralised by the positive particles. There are areas of high positive charge surrounded by larger areas of relatively weak negative charge. If the net charge were evenly distributed then repulsion between particles would lead to a stabilised system¹⁹⁷. However, the large areas of opposing charge on the same particle enable interaction with a similar particle if a positively charged patch on one particle encounters a negatively charged patch on another, thus leading to flocculation. These attractive forces are short range however and unlikely to be a dominant factor at high ionic strength.

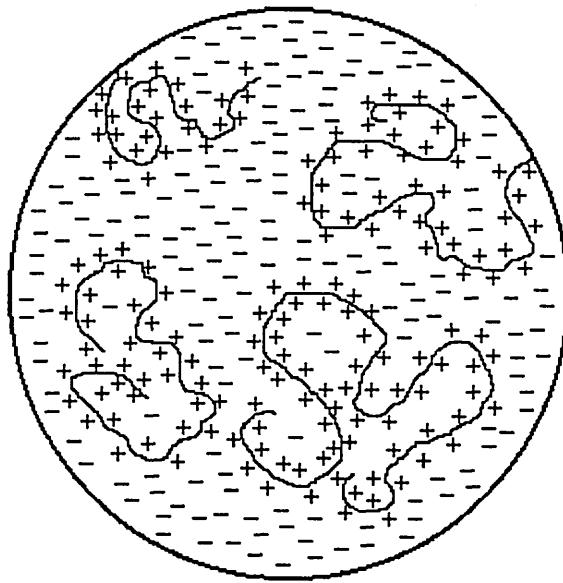


Figure 13. Possible configuration of polycations on a colloidal particle (after Gregory¹⁹⁵).

Figure 14 is a simplistic representation of the electrostatic patch model for a polycation on a negatively charged (clay) particle. **b** and **c** represent repulsive interactions due to facing like charges, with **b** representing the interaction between two areas of negative charge and **c** representing the interaction between two areas of positive charge.

Conversely, **a** represents an attractive interaction between a positively charged area and a negatively charged area.

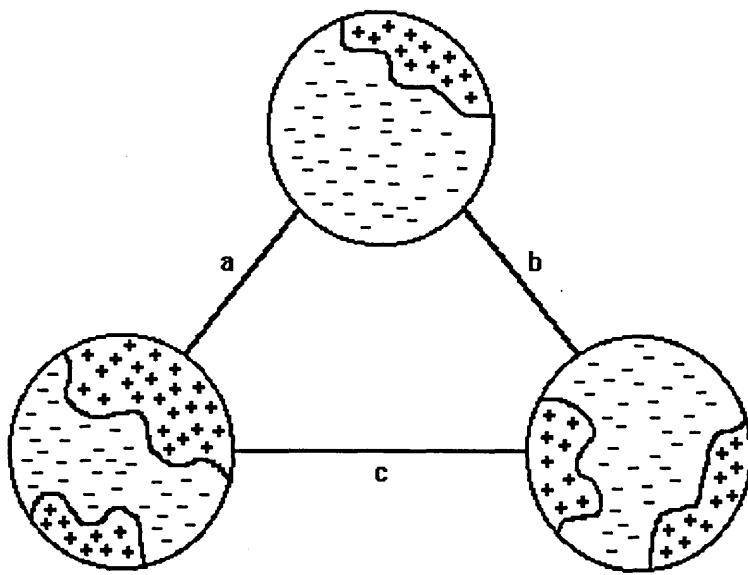


Figure 14. Simplistic representation of the electrostatic patch model of particle flocculation (after Mabire¹⁸⁶). (a) is an attractive interaction while (b) and (c) are repulsive interactions.

3.12 ACID TREATED CLAYS.

3.12.1 Applications.

The use of proton exchanged, or acid treated clay, for use in catalysis is now well documented. Their significant application until the 1960s was as cracking catalysts¹⁹⁸. They then found other industrial uses in processes such as the alkylation of phenols¹⁹⁹, and the dimerisation and polymerisation of unsaturated hydrocarbons²⁰⁰. Recent innovations include the use of Ti^{IV} exchanged acid leached clays as Diels-Alder catalysts²⁰¹ and acid treated clays pillared with oxyhydroxyaluminium species as both catalysts^{202,203} and as selective adsorbents for oil clarification²⁰⁴.

As a result of commercial utilisation of acid treated clays for decolourising oils and in colour formation with leuco-dyes in pressure sensitive recording paper^{21,205}, the effect of acid attack on properties such as surface area and decolourising ability have been widely studied^{19,20,206}.

3.12.2 Activation Treatments.

The acid treatments of clay minerals which modify their surfaces are usually called 'activation treatments' if they produce an increase in the specific surface area and/or in the number of acid centres, elimination of mineral impurities, removal of metal-exchange cations and proton exchange. Appropriate acid and thermal treatments increase the catalytic and adsorbing ability of some clay minerals but further and stronger treatments decrease this activity²⁰⁷.

Treatment of clay with mineral acids is the most widely used technique to impart acidity to the clay surface. Commercial products are normally treated with a fixed amount of acid which is sufficient to remove only that number of octahedral cations required to optimise the surface area and Brønsted acidity for a particular application. Although a few investigations on the effect of mineral acid on the chemical structure of the clay have been reported in the past^{23,208,209} studies depicting the correlation of surface acidity and texture with structural changes are sparse²¹⁰. Some workers have shown that the extent of acid attack requires optimisation if the clay is to be used as an effective catalyst^{25,211} but there is still considerable disparity with regard to acid type and concentration, treatment times and source clays studied. The acid treatment of many different clay minerals have been studied, mainly with a view to maximising the intrinsic catalytic

activity of these solid acid catalysts towards petroleum cracking reactions. Acid hydrolysis reactions have been investigated as routes to high surface area silicates with properties well suited as adsorbents, catalysts, and composite filling materials^{212,213,214}.

3.12.3 The Effect of Acid Treatment on the Clay Structure.

It is now generally accepted that montmorillonites with high magnesium contents in the octahedral layer are leached more readily than those containing a higher proportion of aluminium^{215,216,217,218,219}. This has been supported by recent studies of saponite²²⁰ and hectorite²²¹, both minerals with high octahedral magnesium content, which have shown that mild acid treatments at, or near, room temperature are sufficient to cause considerable degradation of the host layer. There is little information available however, concerning the influence that substantial quantities of octahedral iron have on the leaching rate or the subsequent catalytic activity^{215,216,222,223}.

The acidity of acid centres, on various forms of smectites, significantly affects their activity as catalyst supports²⁵, and their sorption properties^{24,224,225}. Reaction rates of smectites in acids are dependant on various factors, including impurities if the sample is not pre-purified.

It has been found that treatment of clays with cold, dilute acid results in an essentially proton exchanged clay, as exchangeable cations are immediately replaced with hydrogen ions, and simultaneously aluminium begins to be leached from the central octahedral lattice layer of the clay¹⁹⁸. This mild treatment has little effect on the elemental composition of the silicate surface and the clays also retain their swelling ability. In

addition, the activated clays may undergo an autotransformation reaction^{226,227,228}, i.e. the interchange of adsorbed H⁺ with octahedral Mg²⁺ and Al³⁺. Mg²⁺ and Al³⁺ then move into interlamellar sites. The first effect of this gradual loss of metal ions from the lattice is further delamination of the clay, which further increases the surface area, with the acidity of the clay also being affected. H⁺ and Al³⁺ are catalytically active whereas Mg²⁺ is not. The rate of the autotransformation reaction has been found to be directly proportional to the magnesium content and CEC of the samples²²⁷. The role of temperature and aluminium and/or magnesium in the process of autotransformation has been investigated^{229,230,231}, but again there is little known concerning the role of iron or other cations²³².

Harsh acid treatment, e.g. activation with hot (80 - 95°C), concentrated acid (e.g. 6 M HCl), results in the removal of ions associated with the octahedral sheet and may not produce an exclusively proton exchanged clay. Octahedral cations such as Al³⁺, Fe²⁺, Fe³⁺ and Mg²⁺ can be depleted by treating the clay minerals with acids at elevated temperatures with the rates of depletion usually following the order Mg²⁺ > Fe²⁺ > Fe³⁺ > Al³⁺^{233,234}. Ions removed from the octahedral sheet may take up interlamellar exchange positions. The rate of leaching increases rapidly as the temperature is increased and the extent of octahedral sheet depletion increases with the time of treatment^{235,236}. Maximum catalytic activity is associated with harsh treatments so that a large proportion of the lattice aluminium is removed²¹¹. However, depletion of the octahedral sheet causes a reduction in the number of cation-exchange sites which is where the protons reside, with a concomitant loss in catalytic activity²¹⁸. The product of completed dissolution is amorphous, three dimensional silica which has a low surface area and no catalytic activity²³⁷.

The adsorption capacity of an acid-activated clay may peak either before or after the achievement of maximum surface area, depending on the exact origin of the clay¹⁹. The adsorptive properties of such activated clays depend on the chemical nature of the clay surface and the sorption process is influenced by the electrostatic interaction between the adsorbate molecules and the adsorption sites on the clay surface, the nature of the exchangeable cation occupying the interlayer region of the clay, and the extent to which the cation is hydrated.

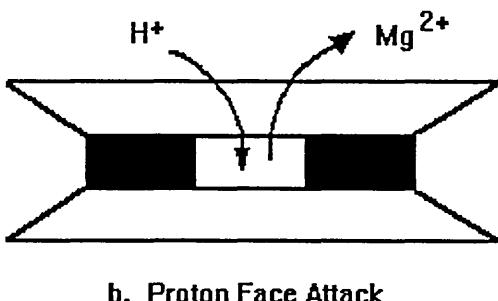
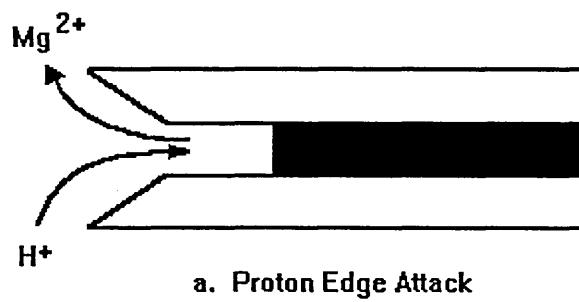


Figure 15. Showing the depletion of octahedral Mg^{2+} from 2:1 layered silicates by (a) Proton Edge Attack and (b) Proton Face Attack.

The mechanism for depletion of metal ions from the octahedral sheet of 2:1 swelling clays involves proton attack at (i) the edges of the clay layers and (ii) through the ditrigonal cavities of the basal surfaces wherein protons can easily occupy the interlamellar surfaces by ion exchange²³⁸. Figure 15 shows these two mechanisms.

Evidence for edge attack is provided in part by the dependence of hydrolysis rates on the particle size of a non-swelling clay²³⁹. If the swelling ability of the clay is reduced via the Hofman-Klemen effect⁵⁵, or by exchange with long chain alkylammonium ions, then only edge attack occurs.

3.12.4 Measurement of Structural Changes and Acidity.

Acidic and basic sites of different natures and with different strengths, appear together on the clay surface and they determine the bulk acidity of the natural mineral. The basicity of the oxygen plane of the silicate layer is determined by possible interactions between the oxygen atoms of the siloxane groups and acidic species which tend to accept electron pairs. The acid can be of either Brønsted (proton donating) or Lewis (electron accepting) type. For this to happen the siloxane oxygen atom must donate a lone pair of electrons to an acceptor. A $d\pi-p\pi$ bond is found between O and Si in Si-O-Si and Si-O-Al groups. Partial π interaction between oxygen and silicon atoms causes the oxygen atom to serve as a weak base. Also, tetrahedral substitution of Si^{4+} by Al^{3+} leads to changes in the clay surface properties, resulting from an increase in the basic strength of the siloxanes. There is much evidence showing that this substitution leads to an increase in both types of surface activity, acceptance and donation of electron pairs. The increase in acidic activity is explained by the presence of additional exchangeable cations⁷⁹. Also, octahedral substitution of Mg^{2+} by Al^{3+} increases the polarisation of the OH planes. Interactions occurring between the oxygen plane and acid sites in the interlayer space of smectites affect the bulk surface acidity of the interlayer and the type of reactions which occur between the clay and adsorbed organic acids and bases. Clays with tetrahedral substitution form π bonds by donating electrons to aromatic cations and radicals.

In pure montmorillonite, the water of hydration is the main source of Brønsted acidity.

Deuteration of lattice hydroxyls proceeds rapidly in the presence of D₂O and Lewis acidity may be present²⁴⁰.

Acid dissolution of clays can provide useful information on the reactivity of the mineral involved, e.g. kinetic parameters²⁴¹ or characteristics of reactants and reaction products^{237,242}. It is well known that acid treatment provides an increase in surface area and porosity, but little is known about the structural changes which accompany acidification, largely because the reduced crystallinity associated with extended acid treatment precludes observation of resolved XRD patterns.

Two widely used methods for the determination of the number of acid sites present depends on the adsorption of bases, either from the gas phase or from the liquid phase (non-aqueous solutions). The most widely used bases are ammonia, pyridine or aliphatic amines. When chemisorbed on surfaces possessing acidic properties, amines can interact with acidic protons, electron acceptor sites and protons from neutral or weakly acidic hydroxyl groups²⁴³. Thermal desorption and differential scanning techniques can measure the presence of such bases which may be related to the number of acid sites²³. The majority of catalysts used in this thesis are pre-treated with organic cations which co-evolve with such bases, thus making such thermal techniques impractical.

Infrared spectroscopy (IR) has also been widely applied for the determination of the nature of interactions between the adsorbed bases and the acidic surfaces of the solid²⁴. Structural changes in acid-treated smectites can also be directly studied by IR^{218,219}. There is a complex adsorption band due to the Si-O stretching vibrations of untreated

smectites at approximately 1040 cm^{-1} . With increasing acid dissolution this band shifts to higher wavenumbers (free silica is found at 1100 cm^{-1}), and changes shape²⁴⁴. The increasing amount of amorphous silica with acid dissolution is also reflected in the increase in a band at 795 cm^{-1} . The decomposition of the octahedral sheet by acid treatment is reflected mainly in the IR spectra in the $930\text{-}400\text{ cm}^{-1}$ region which contains bands due to OH bending vibrations, Al-Al-OH at 918 cm^{-1} , Al-Fe-OH 880 cm^{-1} , Al-Mg-OH 843 cm^{-1} as well as Al-O-R 625 cm^{-1} and Al-O-Si 522 cm^{-1} ^{217,244}. These bands gradually decrease in intensity as dissolution proceeds.

Numerous attempts have been made to quantify sources of acidity in pure clays, as well as in soils by means of titration curves^{245,246}. Potentiometric and conductometric titrations with a series of bases have been used to differentiate H^+ from Al^{3+} at the clay surface^{226,229,247}. More recently, multi-nuclear MAS NMR has been used to advantage in the investigation of the extent of acid attack on the aluminosilicate layer^{25,218,219,228}.

3.12.5 Ion Exchanged Catalysts.

In an attempt to increase the catalytic activity of acid-treated clays, exchange with (i) metal cations, and (ii) hydroxy-metal polycations (known as pillars), have been investigated. The cation exchange of clays has been discussed previously in this thesis (Section 2.3) so the main findings will be discussed here.

3.12.5.1 Metal Cations.

Clays have been exchanged with both divalent and trivalent metal cations to improve catalytic activity for synthetic organic reactions and for applications where the clay is

required to act as a solid source of protons. It has been found that clays exchanged with highly polarising cations such as Al^{3+} show the most activity^{22,248}. Although, Ballantine *et al.*²⁴⁹ found that Ni^{2+} and Co^{2+} exchanged smectites showed up to 80% of the activity of the Al^{3+} analogue for (i) the esterification of hex-1-ene with acetic acid, and (ii) the formation of dicyclohexylamine from cyclohexylamine. Breen²⁴ studied the acidity of Ni^{2+} and Co^{2+} exchanged montmorillonite via the desorption of butylamine, cyclohexylamine and pyridine and found that the clays contained predominantly Lewis acid sites, which is in contrast to the type and acidity exhibited by trivalent cation-exchanged clays.

3.12.5.2 Pillars.

The intercalation of smectites with hydroxy-metal polycations is a method of mineral modification which was developed in the late 1970s^{250,251,252}. The method involves the introduction of large metal polycations into the interlayer spaces of clay minerals using ion exchange from aqueous solutions. The polycations act as ‘pillars’ supporting the layers and additionally, after calcination, make the structure rigid. After heat treatment the hydroxycation pillars are converted to oxide pillars²⁵³ which are fixed to the layers of the clay to yield rigid cross linked materials.

The catalytic properties of the pillared clays are a result of the propping apart of the clay structure thereby increasing the surface area and pore volume and exposing much of the interlayer region and any acid sites within to reactant molecules. Furthermore, in addition to expanding the layer structure, Bodoardo *et al.*²⁴⁰ have recently reported that the metal oxide pillars themselves contribute a significant number of Brønsted acid sites.

Pillared interlayer clays (PILCs) have now become an important family of shape-selective catalysts since they combine a tuneable acidity, regular porosity and relatively high thermal stability. The synthesis of different PILCs and their catalytic properties in a variety of chemical reactions have been investigated in detail and reviewed by several authors^{254,255} however, much less information is available concerning the nature of their acid sites²⁵⁶.

The combination of exposing the host clay sheets as well as the presence of the pillars yield materials which possess both Lewis and Brønsted acid sites. The generally accepted view of the acidity of pillared clays is that Lewis acid sites are mainly resident on the metal oxide pillars whereas Brønsted acid sites are associated with structural -OH groups present on the layers of the host clay²⁵⁷. IR studies of pyridine molecules adsorbed on pillared clays have shown that Brønsted acid sites are thermally less stable since the presence of Brønsted sites is lost at temperatures above 300 - 400°C, although at high temperatures (i.e. 400 - 500°C), the acidity of pillared clays is predominantly of the Lewis type²⁵⁸.

To explain the poor activity at low temperature, Tennakoon *et al.*²⁵⁹ proposed that the protons of pillared montmorillonite are locked within the clay sheet and are thus unavailable for catalysis in the interlamellar region. Also, the study of Brønsted sites in PILCs encounters problems since water interacts strongly with the clay and a considerable portion of the hydroxyl groups are hydrogen-bonded. Hence, isolated OH-groups that are considered as active sites in catalysts are hardly visualised in the fundamental region of the IR-spectra due to the background of H-bonded hydroxyls²⁶⁰.

Recently Jones *et al.*^{202,203,261,262} have investigated pillared acid-activated clays. They have shown that acid-activation of a clay matrix prior to the intercalation of alumina pillars results in a thermally stable, porous product²⁶³. These alumina-pillared acid-activated clays (designated Al-PAACs) have been compared to conventional Al PILCs^{203,264} and were found to exhibit increased catalytic activity for butanol dehydration, conversion of cumene and the dehydration of pentanol^{202,203,265}.

While alumina-pillared clays have been shown to be predominantly microporous²⁵², titania pillared clays exhibit significant amounts of mesoporosity²⁶⁶. Yoneyama *et al.*²⁶⁷ have investigated the photocatalytic properties of TiO₂ when incorporated as pillars in montmorillonite and found the activities to be greater for the pillared clay than for the TiO₂ powder particles in the decomposition of propan-2-ol and a number of carboxylic acids. However, despite the promising properties, the use of titania as a pillaring species in clays has been limited by the lack of reproducibility in the preparation of Ti-pillared clays which are frequently poorly ordered compared to their alumina counterparts^{268,269}. Using a new method for preparing Ti-pillared clays, Jones and his co-workers Kooli and Bovey^{261,262} have found that Ti-pillared acid-activated clays (designated Ti-PAACs) possess remarkably enhanced abilities to catalyse the dehydration of pentanol compared with their alumina counterparts (up to 82% enhancement).

3.13 CATALYTIC ACTIVITY.

The ultimate measure of catalytic activity is in the yield of products in the particular reaction of interest. There are numerous reactions for which acid catalysts are used^{22,248}.

The chosen test reaction for this thesis is that of the conversion of α -pinene to camphene and limonene. This will now be discussed.

3.13.1 Acid Catalysis of α -Pinene.

It was stated above (Section 3.12.3), that as clays are acid-activated, octahedral cations such as Al^{3+} , Fe^{2+} , Fe^{3+} and Mg^{2+} can be leached from the structure. Rhodes and Brown²⁷⁰ studied the evolution of catalytic activity as the extent of acid leaching progressed. They found that reactions involving polar solvents, such as the addition of 2,3-dihydropyran to methanol, were catalysed more efficiently on clays which were only partially leached and were still able to swell in polar solvents. In contrast, reactions involving non-polar solvents, such as the rearrangement of α -pinene to camphene, were catalysed more efficiently by clays which were extensively leached and the surface was almost hydrophobic silica.

It was this work of Rhodes and Brown²⁷⁰ that prompted the acid catalysed isomerisation of α -pinene as the test reaction for this thesis. A ‘problem’ amongst workers in this field is the use of non-systematic names for reagents and products. This thesis will use the names in common use in accordance with other workers.

A further problematic feature is that of non-uniform experimental conditions. Workers have used different acids and acid concentrations in addition to different times and temperature of reaction which makes direct comparisons difficult.

3.13.2 Applications.

α -Pinene is a member of the monoterpenoids, or terpene groups, of compounds. Terpenes constitute one of the largest groups of industrially important natural products. They occur in essential oils derived from various plants and trees such as coniferae (e.g. turpentine derived from pine trees) and are even found in the curry plant (α -pinene is approximately 17.2% total essential oil)²⁷¹.

One of the main uses of terpenes is in the pharmaceutical industry. α -Pinene, for example, has been found to be a superb candidate for a starting material for the synthesis of taxol since it possesses 10 of the 20 atoms of the carbocyclic core of taxol and is inexpensive²⁷². Taxol (Figure 16) has received approval for the treatment of ovarian cancer and is undergoing further investigation for treatment of other cancer types. The aroma properties of the terpenes are also used in health care and even the perfume industry.

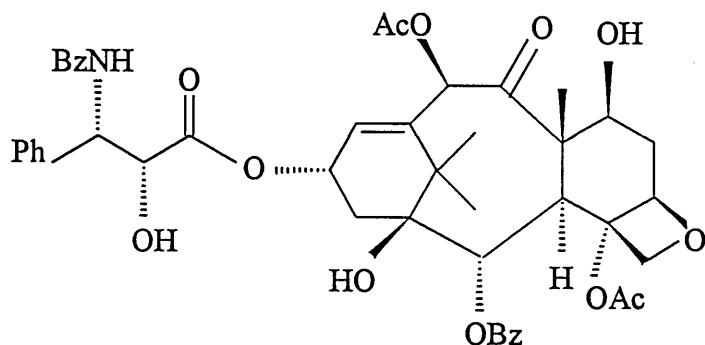


Figure 16. The Structure of Taxol.

There are also other applications. The product mixture from the acid catalysed reaction of cyclic monoterpenes and phenol has found wide use in applications²⁷³ such as thermal transfer receptor sheets, phenolic resin insulators and coatings, hot melt adhesives and epoxyresins.

Recently Hennig *et al.*²⁷⁴ have investigated metal porphyrin complexes as light sensitive precursor compounds for the photocatalytic activation of dioxygen in aqueous solutions. They have found that in the presence of α -pinene and other cycloalkenes, photocatalytic oxygenation reactions occur. An advantage here being that the catalyst may be conveniently separated from the substrates/products by using aqueous solvent systems.

3.13.3 The Rearrangement of α -Pinene.

Studies of the acid catalysed rearrangement of α -pinene began in the 1960s. Early workers such as Williams and Whittaker^{275,276} suggested that the reaction proceeded through a common intermediate stage which involved two equilibrating ions (carbocations). These ions were then thought to undergo ring expansion to give bornane and fenchane derivatives, or ring opening to *p*-menthane derivatives. The former route was favoured in non-aqueous conditions. The products could then undergo subsequent rearrangements.

For the acid catalysed hydration of α -pinene in aqueous 95% acetone containing different concentrations of sulphuric acid, Williams *et al.*²⁷⁵ identified six significant products, namely camphene, limonene, terpinolene, α -fenchol, α -terpineol and borneol. However, in anhydrous acetic acid/sulphuric acid additional products were found²⁷⁶ (e.g.

g-terpinene, *i*-terpinolene, α -terpinylacetate). They surmised that the highly polar protic solvents (e.g. H_2SO_4) favour the formation of monocyclic terpenes via formation of the carbocation intermediate, whilst less polar solvents (e.g. $OAcH/H_2SO_4$) favour formation of bicyclic terpenes. Figure 17 shows products of the acid catalysed rearrangement of α -pinene (products of hydration are not shown).

It is now generally understood that in the presence of acids α -pinene can ring expand either by shift of the gem-dimethyl bridge to give camphene, or by shift of the methylene bridge to give α -fenchene. Alternatively, the ring can open to give a mixture of the *p*-menthadienes, mainly limonene, terpinolene and α -terpinene.

3.13.4 Other Solid Catalysts Used for the Conversion of α -Pinene.

Over solid catalysts such as clays, mineral oxides and inorganic salts the main product is often camphene but this may not be the preferred product. The reactions with clays are on an open surface so do not usually lead to high product selectivity. Selectivity may be improved by carrying out the reaction in a constrained pore, i.e. by the use of zeolites.

The production of camphene may be carried out by isomerisation of α -pinene over titanium oxide catalysts²⁷⁷. These catalysts are prepared by treating titanium oxide with an acid in order to obtain a layer of titanic acid on the surface of the oxide. Camphene is of particular interest as an intermediate in the synthesis of camphor which in turn is of value due to its aroma and pharmaceutical properties.

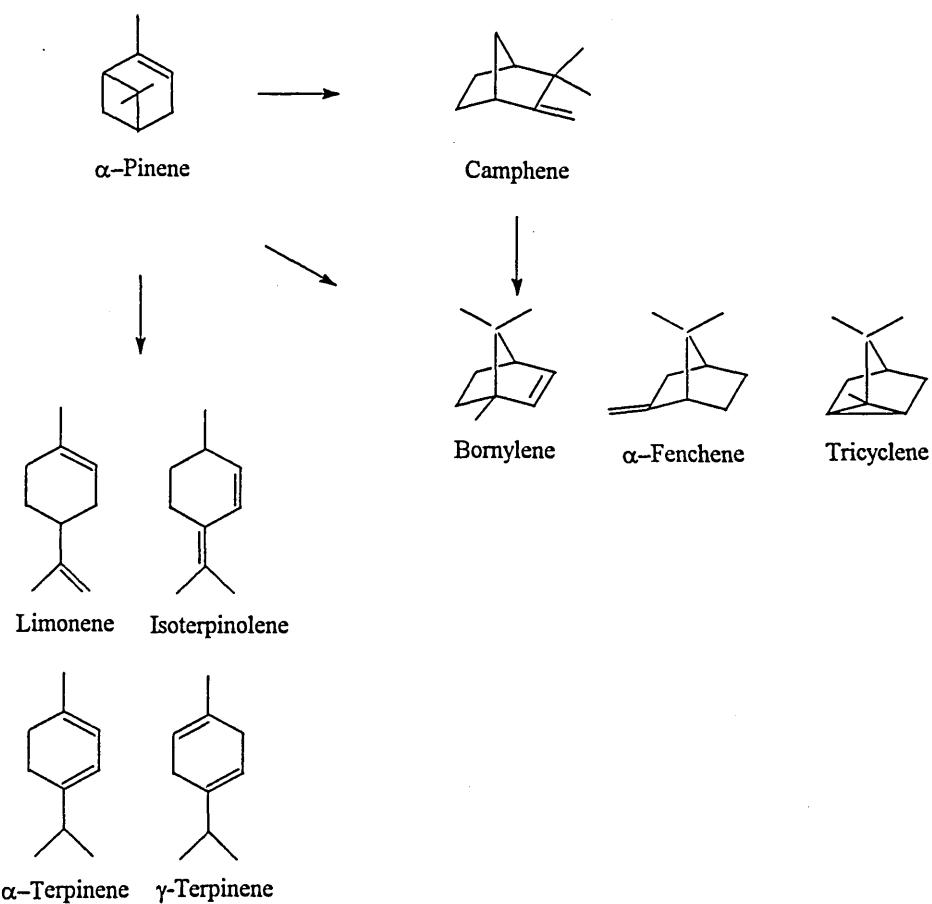


Figure 17. Products of the acid catalysed rearrangement of α -pinene (products of hydration are not shown).

De Stefanis *et al.*²⁷⁸ have investigated the reaction of α -pinene over several PILCs, a layered α -tin phosphate analogue (Al-PILP), H^+ -mordenite and two mid pore zeolites namely USY and NH_4^+ -ZSM-5 (with SiO_2/Al_2O_3 ratios = 35 and 235). They carried out their reactions under Lewis acid conditions (i.e. each solid was first activated to remove all water), at 100°C for 5 hours. They achieved 42 - 48% conversion of α -pinene to camphene for USY (42%), BP-PILC (45%) and FAZA (48%) (an iron-alumina-pillared mixed beidellite-montmorillonite), and up to 13% conversion to limonene, USY (selective against limonene, therefore 0%), BP-PILC (13%), FAZA (12%). H^+ -

mordenite, although more acidic than BP-PILC and FAZA, produced only 29% camphene, but 17% limonene.

Recently van der Waal *et al.*²⁷⁹ investigated the hydration and isomerisation of α -pinene over zeolite H-beta. They reported that in the presence of water the main product is α -terpinol (48%) (monocyclic alcohol) though selectivity towards bicyclic terpenes is higher than observed for sulphuric acid (26% vs. 5.5%), with camphene being the predominant product. They also found that when the isomerisation is performed in pure acetone, a new compound, identified as α -terpinyl acetone, forms by a C-C coupling reaction between α -pinene and acetone. The coupling seems to be a general reaction between α -pinene and ketones but is only catalysed by zeolite H-beta.

Also recently, Cruz Costa *et al.*²⁸⁰ have studied the gas-phase rearrangement of α -pinene catalysed by metal (IV) phosphate polymers. They found that the phosphates catalyse carbocation rearrangements as expected from the results of other workers as discussed above. They also observed catalysis of a modified radical rearrangement of α -pinene to yield α -pyronene. The main thermal decomposition/rearrangement products were limonene, and α -pyronene.

Krishnasamy *et al.*²⁸¹ investigated the dehydrogenation of α -pinene over alumina and platinum-alumina catalysts in the vapour phase. They found that the initial isomerisation to the intermediate ions took place over the acidic sites of the alumina and not the platinum metal sites. Hence the variation of platinum concentration in the catalysts did not affect the extent of overall conversion.

3.14 SUMMARY OF ACID TREATMENT.

Clay minerals may be acid treated in order to increase their catalytic activity. The reaction rates in smectites are dependant on various factors but montmorillonites with high magnesium contents in the octahedral layer are leached more readily than those containing a higher proportion of aluminium. Mild acid treatment results in an essentially proton exchanged clay which retains its swelling ability and shows little structural decomposition. Maximum catalytic acitivity is associated with harsh acid treatments so that a large proportion of lattice aluminium is removed, although depletion of the octahedral sheet causes a reduction in the number of cation-exchange sites with a concomitant loss in catalytic activity. The extent of structural change and acidity can be measured by a number of techniques including IR, NMR and measurement of the desorption of bases.

The catalytic activity of acid treated clays can be increased by exchange with divalent or trivalent metal cations or with large hydroxy-metal cations (pillars). The ultimate measure of catalytic activity is in the yield of products in the particular reaction of interest, which in this thesis is the conversion of α -pinene to camphene and limonene. The yields obtained herein will be compared with those reported in the 1

CHAPTER 4

Experimental Techniques, Equipment and Sample Preparation.

4. INTRODUCTION.

Consideration of the available literature, as reviewed in Chapter 3, led to the application of the experimental procedures presented in this Chapter.

4.1 CLAY MINERALS INVESTIGATED.

The clay minerals chosen for use in this study are as summarised in Table 4.

Clay type	Abbreviation	Origin
*Ca-montmorillonite 'Cheto'	SAz-1	Apache County Arizona, USA.
*Na-montmorillonite	SWy-2	Crook County, Wyoming.
*Hectorite	SHCa-1	San Bernado County, California, USA.
*Saponite	SapCa-1	Ballarat, California.
*Al-montmorillonite 'Jelsovy Potok'	JP	Kremnica mountains, Central Slovakia.***
* Beidellite 'Stebno'	ST	Czech Republic.***
*Nontronite	SWa-1	Grant County, Washington, USA.***
** Westone-L montmorillonite	WL	Texas, USA.
** Westone-L3 montmorillonite	WL3	Texas, USA.

*Supplied by the University of Missouri, Columbia, Source Clay Minerals Repository.

**From ECC America Inc., Southern Clay Products Subsidiary.

*** Supplied in the exchanged form by co-workers in Bratislava.

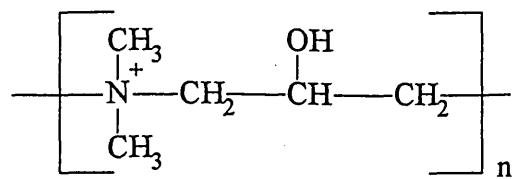
Table 4. Describing the clays used in this work.

4.1.1 Sedimentation / Purification and Ion Exchange.

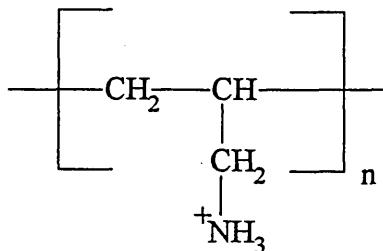
The clays used in the majority of experiments have undergone no purification procedures as this represents the case for many of the suggested applications ‘in-situ’. However, some comparative studies have been carried out with purified clays. In particular, the clays supplied by the co-workers in Bratislava have been extensively purified. Sedimentation removes impurities such as iron oxide, quartz and mica and produces a clay fraction of < 2 µm particle size.

Raw clay was sedimented by suspending a quantity (0.5 kg) in deionised water (10.0 L), allowing the suspension to settle for 16 hours then collecting, by siphoning, the top 0.1 m. More deionised water was added to the bulk, the clay was resuspended and the process repeated 3 to 4 times.

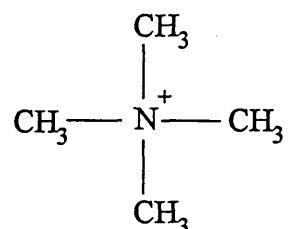
The clay (sedimented or not) may be ion exchanged by washing with a salt solution containing the appropriate ion. For example, in some experiments WL (Westone-L) has been sodium exchanged by immersion in 1.0 M NaCl solution. The clay was resuspended in the salt solution by homogenisation, centrifuged and the supernatant discarded. The clay was resuspended in a fresh salt solution and the process repeated three times in all. Any excess ions were removed by a similar washing process but using deionised water in place of the salt solution. Washing continued until the conductivity of the supernatant was < 20 µS. Finally, the exchanged clay was resuspended to give a concentration of 50 g/L. Caesium exchanged WL has been prepared in a similar manner using CsCl. XRF analysis is used to confirm that the clay is saturated with the ion of interest.



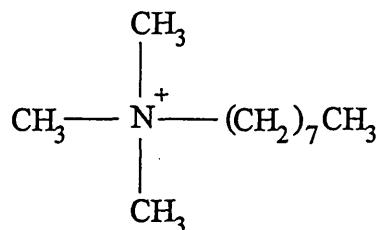
a.



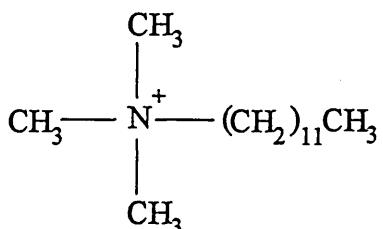
b.



c.



d.



e.

Figure 18. a. The monomer unit of Magnafloc 206 (Cl^- counter ions), b. poly(allylamine hydrochloride), c. tetramethylammonium chloride, d. octadecyltrimethylammonium bromide, e. dodecyltrimethylammonium bromide. (The Cl^- and Br^- counter ions are not shown).

4.2 TERMS OF ABBREVIATION.

Clay which has not been subjected to cation exchange procedures will be termed heterionic. The sodium exchanged Westone-L will be referred to as Na-WL, similarly caesium exchanged Westone-L will be referred to as Cs-WL.

4.3 ORGANIC ADSORBATES.

The main polymer used in this work has been supplied by Allied Colloids and is known as Magnafloc 206 (Figure 18a), and has a molecular weight of 50,000. It is synthesised by copolymerising diethylamine and epichlorohydrin and contains 9% nitrogen by weight as confirmed by Kjeldahl analysis. It was supplied 50% active (i.e. diluted with water by 50%), and was further diluted 10 fold before an aliquot was contacted with the clay.

Poly(allylamine hydrochloride), (hereon referred to as PAA), (Figure 18b) treated SWy-1 has been studied for its potential as an adsorbent of *p*-nitrophenol. PAA, (molecular weight 50,000 - 65,000) was supplied (Aldrich) in rod form and was diluted in deionised water before being added to the clay in appropriate amounts. In comparison with Magnafloc, PAA contains no OH groups and should be entirely hydrophobic so PAA-SWy-1 was anticipated to be a better adsorbent than Magnafloc 206 exchanged SWy-1.

The adsorption of TMA⁺ (Figure 18c) by clay has also been studied. Stock solutions of tetramethylammonium chloride (1.0 M) were prepared before being added to the clay of interest in appropriate amounts.

The clays supplied by co-workers for catalysis work were pre-exchanged with tetramethylammonium (Figure 18c), octadecyltrimethylammonium (Figure 18d) and dodecyltrimethylammonium (Figure 18e) ions, as described in Section 4.6 below.

4.4 ANALYSIS TECHNIQUES USED TO INVESTIGATE THE INTERACTION BETWEEN THE CATIONIC ORGANIC SPECIES AND CLAY.

4.4.1 X-Ray Fluorescence Analysis.

X-Ray Fluorescence Analysis (XRF) was used to determine the elemental composition of the clay. Each sample was ground into a powder and dried at 120°C. The dried clay (1.0 g) was mixed with powdered lithium-tetraborate (10.0 g), put into a platinum crucible and heated at 1250°C for 6 minutes. The mixture was then swirled to improve mixing, heated for a further 6 minutes, poured into a mould and allowed to solidify before analysis. A Philips PW 2400 XRF spectrometer was used for all analyses.

4.4.2 Kjeldahl Nitrogen Analysis.

Kjeldahl nitrogen analysis was used to determine the amount of N containing (poly)cation adsorbed by the clay, by analysing for the total organic nitrogen content in the sample.

4.4.2.1 Sample Preparation.

Poly(cation) containing samples were prepared by contacting, in a low density polyethylene bottle, 10 ml of 50 g/L clay (i.e. 0.5 g), an amount of the (poly)cation and sufficient deionised water to give a total volume of 20 ml. The deionised water was added to the clay prior to the (poly)cation. Each sample was then oscillated at 280

r.p.m. at 28°C in a New Brunswick gyrotary water bath shaker for two hours. After centrifuging for 20 minutes at 20,000 r.p.m. the supernatant was decanted and the clay resuspended in 25 ml deionised water to wash off any unabsorbed species. The clay was centrifuged once more then dried at 120°C overnight, ground into a powder and stored at room temperature.

4.4.2.2 Sample Digestion and Analysis.

Known weights of dried (> 2 hours at 120°C) clay were digested in a Kjeldahl digestor containing two catalyst tablets (94% K₂SO₄, 5.5% CuSO₄.5H₂O, 0.5% Se), and 25 ml H₂SO₄ (98%, low in nitrogen). This was heated to 380°C for four hours. Samples were then analysed in a Gerhardt Vapodest Kjeldahl Autoanalyser. The total nitrogen content of the sample was automatically calculated following (i) addition of 40% NaOH (30ml) which made the solution basic; (ii) the NH₄⁺ in solution was converted to NH₃ and steam distilled before adsorption into a 4% boric acid solution; (iii) the complex so formed was then titrated with 0.1 M HCl. The percentage nitrogen by weight was thus calculated.

4.4.2.3 Reproducibility of Kjeldahl Nitrogen Analysis.

Reproducibility studies were carried out by determining the nitrogen contents of TMA⁺ exchanged SAz-1, SWy-1 and WL, and of the same clays with high loadings of polymer on (a) 3 consecutive days, (b) 5 days chosen at random to include a range of atmospheric conditions. Also, the nitrogen content of ammonium sulphate, which is soluble in water and so does not require digestion, was measured at least twice each

time the Autoanalyser apparatus was operated. This served as a standard and indicator of any operation problems. Nitrogen contents were found to be $\pm 0.100\%$.

Clays exchanged with other nitrogen containing organic cations may also be analysed by the Kjeldahl technique, even if they have been prepared by a different method, assuming they can be suitably digested.

4.4.3 X-Ray Diffraction Analysis.

X-Ray Diffraction Analysis (XRD) was used to determine how the polycation was associated with the clay, i.e. whether the polycation was adsorbed onto the surface of the clay or whether it resided between the clay platelets. This information was found from monitoring changes in the d-spacing of the first order basal reflection (d_{001} spacing) of the clay/polymer complex. The thermal stability of the complexes was determined by measuring the d-spacing at elevated temperatures (from ambient to 250°C). All samples were prepared by pipetting a small amount of the clay suspension of interest onto a glass slide and allowing to dry. Slides prepared for comparative studies were all taken from the same point in sample preparation, e.g. polycation exchanged clay samples are prepared as for Kjeldahl analysis but a small amount was pipetted onto a slide after 2 hours shaking (Section 4.4.2.1).

The glass slide was then placed on a simple heating stage and heated from $50 - 250^{\circ}\text{C}$ in increments of 50°C . Samples were held at these temperatures for 30 minutes prior to recording the XRD trace to enable equilibrium to be reached. A Philips PW1140 X-ray diffractometer using $\text{CuK}\alpha$ radiation was used for all analyses. The voltage and current

used in all analyses was 40 kV and 20 mA respectively. All traces were recorded from 4° to 35° at increments of 0.04° every 2 seconds.

4.4.4 Thermogravimetric Analysis.

Thermogravimetric (TG) analysis is another technique used to determine the thermal stability of the clay/polymer complex and to corroborate the results obtained by Kjeldahl analysis. In this method the weight of the sample was monitored as the temperature was increased. Samples were prepared as for Kjeldahl analysis (Section 4.4.2.1) but a small amount of the dried clay is reserved for corroboration by TG analysis. 6 - 10 mg of the sample was weighed into a ceramic crucible, placed into the heating chamber and purged with dry nitrogen gas (20 ml/min) for 20 minutes or until constant sample weight was obtained. Samples were then heated from 35 - 800°C at 20°C/min under a flow of 20 ml/min dry nitrogen carrier gas and the change in weight was automatically recorded. A Mettler TG 50 thermobalance equipped with a TC10A processor was used for all analyses.

4.4.5 % Carbon Analysis.

% Carbon values were obtained by the co-workers in Bratislava on a CHN analyser, Fisons Instruments EA 1108.

4.5 CLAY PREPARATION FOR POLLUTION ADSORPTION STUDIES.

Unsedimented, heterionic clays were prepared in the same manner as for the Kjeldahl samples (Section 4.4.2.1), with sufficient (poly)cation added to produce the extent of exchange required. For adsorption studies, TMA-clays were prepared by adding 5

times the CEC of TMA^+ to the clays to ensure complete exchange. TMA^+ adsorption showed a steep rise until 90% of the CEC sites are occupied, then a more gradual slope until all sites are occupied (Figure 20). The resultant organoclays were then dried before use. Hereafter, TMA^+ exchanged SAz-1 and SWy-1 will be referred to as TMA-SAz-1 and TMA-SWy-1, respectively.

The adsorption of (a) benzene and (b) *p*-nitrophenol has been studied for clays (i) fully exchanged with TMA^+ , and (ii) exchanged with varying amounts of polymer. The amounts of polymer were chosen from different regions of the uptake curves (Figure 21, Chapter 5), to represent different extents of polymer loading.

4.5.1 Techniques for Measurement of Pollutant Adsorption.

4.5.1.1 Gas Chromatography.

Gas chromatography (GC) was used to monitor the uptake of benzene onto the clay-(poly)cation complex. A range of benzene concentrations were used between 0 - 1.2 mg/ml. The powdered organoclay (200 mg) and benzene solution (25 ml) were placed into sealed glass bottles and oscillated at 280 r.p.m. at 28°C for 12 hours. The bottles were centrifuged at 4000 r.p.m. for 30 minutes. 1 ml of the benzene solution (supernatant) was then added to 1 ml toluene solution (0.5 mg/ml). The toluene acts as an internal standard in the chromatograms. Control samples containing the benzene solutions but no clay were made to monitor recoveries (80 - 85%). The solutions were then analysed on a Fractovap Series 2150 gas chromatograph using a flame ionisation detector and a Varian 4270 integrator. The conditions are given in Table 5. A packed

column, containing Waters Poropak Q-S mesh size 80-100, with nitrogen carrier gas, was used for all separations.

Oven temperature	200°C
Isothermal	25 minutes
Injector temperature	225°C
Detector temperature	225°C
Hydrogen pressure	0.8 kg/cm ²
Air pressure	1.0 kg/cm ²
Nitrogen pressure	2.2 kg/cm ²

Table 5. Conditions employed for GC analysis of benzene uptake.

4.5.1.2 Ultra-Violet Spectrophotometry.

Ultra-Violet Spectrophotometry (UV) was used to monitor the uptake of *p*-nitrophenol onto the clay/(poly)cation complexes. 50 mg of the clay/(poly)cation complex was introduced into a sample vial to which was added 10 ml of *p*-nitrophenol solution, of known concentration, buffered at pH 4 (0.05 M potassium hydrogen phthalate). A range of concentrations between 0 - 1.5 mg/ml was used. Each sample was then oscillated at 280 r.p.m. at 28°C for 12 hours then allowed to settle. 1 ml of the *p*-nitrophenol solution above the clay was then mixed with 10 ml NaOH (0.01 M) to achieve pH 9 to give a measurable signal since at pH 9 *p*-nitrophenol is converted to the yellow *p*-nitrophenoxide ion. Measurements are made at 400 nm. A Unicam ATI UV/Visible Spectrometer, UV/2 was used for all analyses.

4.5.1.3 Reproducibility of Pollutant Adsorption Determinations.

Reproducibility studies have been carried out by determining the uptake of pollutants by TMA-SWy-1 and TMA-SA_z-1 on (a) four consecutive days, and (b) five days chosen at random to include a range of atmospheric conditions. Hence, values quoted for the uptake of benzene from solution are ± 2.5 mg/g and for *p*-nitrophenol are ± 2.0 mg/g.

4.6 CLAY PREPARATION FOR CATALYTIC STUDIES.

The majority of organoclays studied for catalysis were prepared in the same manner as for the Kjeldahl samples (Section 4.4.2.1), with sufficient (poly)cation added to produce the extent of exchange required. Again, TMA-clays were prepared by adding 5 times the CEC of TMA⁺ to the clays to ensure complete exchange (Section 4.5). The dried clays were then acid-activated to differing extents as shown in the tables at the end of this section (Tables 7 - 11). After acid treatment the clays were gravity filtered, and washed with 25 ml deionised water. After centrifuging for 20 minutes at 20,000 r.p.m. the supernatant was decanted and the clay resuspended in 25 ml deionised water to remove any residual acid. The clay was centrifuged once more then air dried, ground and stored at room temperature.

Co-workers in Bratislava prepared ODTMA⁺ and DDTMA⁺ and also TMA⁺ exchanged clays. Prior to exchange with the organic cations, coarse samples of JP, SWa-1 and ST were suspended in deionised water, treated five times with 1.0 M aqueous calcium chloride then washed until free of chloride. The samples were then centrifuged, and the nominally < 2 μ m sample was collected, dried at 60°C and ground to < 0.2mm prior to organocation exchange and/or acid treatment (Tables 7 - 9). The structural formulae of the purified smectites are given in Table 6.

2.0 g portions of each purified smectite were stirred in deionised water for eight hours and then the required amount of organic salt (tetramethylammonium chloride, octadecylammonium bromide, or dodecyltrimethylammonium bromide) was added in an amount equal to 0.25, 0.50 or 1 (meq organocation)/(g clay). The resulting suspensions were heated at 60°C for three hours with stirring. The samples were then allowed to stand for 24 hours. The supernatant was removed and assayed for displaced Ca²⁺ ions using compleximetric titration. The solids were washed with deionised water until a negative AgNO₃ test for halide was obtained.

Sample	JP	ST	SWa-1
M ^a	0.91	0.95	0.81
Si ^b	7.71	7.22	7.33
Al ^b	0.29	0.78	0.67
Al ^c	3.00	1.96	0.91
Fe ^c	0.38	1.60	2.86
Mg ^c	0.63	0.58	0.28
Li ^c	0.00	0.00	0.00

^a Interlayer cations

^b Tetrahedral cations

^c Octahedral cations

Table 6. Structural formula of smectites in the fine fractions of the samples used.

A summary of the extents of organic cation exchange and acid treatments are given in Tables 7 - 11. As examples, (1) JP-M1-4 is Jelsovy Potok which has been exchanged with 0.25 mmol tetramethylammonium cations/g clay then acid activated in 4 ml 0.1 M HCl at 25°C for 60 minutes, (2) ST-L2-60 is Stebno which has been exchanged with 0.50 mmol dodecyltrimethylammonium cations/g clay then acid activated in 60 ml 1.0 M

Code	Organic cation (OC)	mmol OC offered	Volume HCl (ml)	HCl Concn.	Treatment Temp.	Acid contact time (minutes)
JP-0	None	-----	None	-----	-----	-----
JP-2	None	-----	2	0.1 M	25°C	60
JP-4	None	-----	4	0.1 M	25°C	60
JP-M1	TMA	0.25	None	-----	-----	-----
JP-M2	TMA	0.50	None	-----	-----	-----
JP-M3	TMA	1.00	None	-----	-----	-----
JP-M1-2	TMA	0.25	2	0.1 M	25°C	60
JP-M1-4	TMA	0.25	4	0.1 M	25°C	60
JP-M2-2	TMA	0.50	2	0.1 M	25°C	60
JP-M2-4	TMA	0.50	4	0.1 M	25°C	60
JP-M3-2	TMA	1.00	2	0.1 M	25°C	60
JP-M3-4	TMA	1.00	4	0.1 M	25°C	60
JP-L1	DDTMA	0.25	None	-----	-----	-----
JP-L2	DDTMA	0.50	None	-----	-----	-----
JP-L3	DDTMA	1.00	None	-----	-----	-----
JP-L1-2	DDTMA	0.25	2	0.1 M	25°C	60
JP-L1-4	DDTMA	0.25	4	0.1 M	25°C	60
JP-L2-2	DDTMA	0.50	2	0.1 M	25°C	60
JP-L2-4	DDTMA	0.50	4	0.1 M	25°C	60
JP-L3-2	DDTMA	1.00	2	0.1 M	25°C	60
JP-L3-4	DDTMA	1.00	4	0.1 M	25°C	60
JP-O1	ODTMA	0.25	None	-----	-----	-----
JP-O2	ODTMA	0.50	None	-----	-----	-----
JP-O3	ODTMA	1.00	None	-----	-----	-----
JP-O1-2	ODTMA	0.25	2	0.1 M	25°C	60
JP-O1-4	ODTMA	0.25	4	0.1 M	25°C	60
JP-O2-2	ODTMA	0.50	2	0.1 M	25°C	60
JP-O2-4	ODTMA	0.50	4	0.1 M	25°C	60
JP-O3-2	ODTMA	1.00	2	0.1 M	25°C	60
JP-O3-4	ODTMA	1.00	4	0.1 M	25°C	60

TMA = Tetramethylammonium

DDTMA = Dodecyltrimethylammonium

ODTMA = Octadecyltrimethylammonium

Table 7. Showing the extents of organic cation exchange and acid treatments for Jelsovy Potok (JP) derived samples.

Code	Organic cation (OC)	mmol OC offered	Volume HCl (ml)	HCl Concn.	Treatment Temp.	Acid contact time (minutes)
ST-0	None	-----	None	-----	-----	-----
ST-2	None	-----	2	0.1 M	25°C	60
ST-4	None	-----	4	0.1 M	25°C	60
ST-60	None	-----	60	1.0 M	25°C	60
ST-M1	TMA	0.25	None	-----	-----	-----
ST-M2	TMA	0.50	None	-----	-----	-----
ST-M3	TMA	1.00	None	-----	-----	-----
ST-M1-2	TMA	0.25	2	0.1 M	25°C	60
ST-M1-60	TMA	0.25	60	1.0 M	25°C	60
ST-M2-2	TMA	0.50	2	0.1 M	25°C	60
ST-M2-60	TMA	0.50	60	1.0 M	25°C	60
ST-M3-2	TMA	1.00	2	0.1 M	25°C	60
ST-M3-60	TMA	1.00	60	1.0 M	25°C	60
ST-L1	DDTMA	0.25	None	-----	-----	-----
ST-L2	DDTMA	0.50	None	-----	-----	-----
ST-L3	DDTMA	1.00	None	-----	-----	-----
ST-L1-2	DDTMA	0.25	2	0.1 M	25°C	60
ST-L1-60	DDTMA	0.25	60	1.0 M	25°C	60
ST-L2-2	DDTMA	0.50	2	0.1 M	25°C	60
ST-L2-60	DDTMA	0.50	60	1.0 M	25°C	60
ST-L3-2	DDTMA	1.00	2	0.1 M	25°C	60
ST-L3-60	DDTMA	1.00	60	1.0 M	25°C	60
ST-O1	ODTMA	0.25	None	-----	-----	-----
ST-O2	ODTMA	0.50	None	-----	-----	-----
ST-O3	ODTMA	1.00	None	-----	-----	-----
ST-O1-2	ODTMA	0.25	2	0.1 M	25°C	60
ST-O1-60	ODTMA	0.25	60	1.0 M	25°C	60
ST-O2-2	ODTMA	0.50	2	0.1 M	25°C	60
ST-O2-60	ODTMA	0.50	60	1.0 M	25°C	60
ST-O3-2	ODTMA	1.00	2	0.1 M	25°C	60
ST-O3-60	ODTMA	1.00	60	1.0 M	25°C	60

TMA = Tetramethylammonium

DDTMA = Dodecyltrimethylammonium

ODTMA = Octadecyltrimethylammonium

Table 8. Showing the extents of organic cation exchange and acid treatments for Stebno (ST) derived samples.

Code	Organic cation (OC)	mmol OC offered	Volume HCl (ml)	HCl Concn.	Treatment Temp.	Acid contact time (minutes)
SWa-0	None	-----	None	-----	-----	-----
SWa-2	None	-----	2	0.1 M	25°C	60
SWa-4	None	-----	4	0.1 M	25°C	60
SWa-60	None	-----	60	1.0 M	90°C	60
SWa-M1	TMA	0.25	None	-----	-----	-----
SWa-M2	TMA	0.50	None	-----	-----	-----
SWa-M3	TMA	1.00	None	-----	-----	-----
SWa-M1-2	TMA	0.25	2	0.1 M	25°C	60
SWa-M1-60	TMA	0.25	60	1.0 M	90°C	60
SWa-M2-2	TMA	0.50	2	0.1 M	25°C	60
SWa-M2-60	TMA	0.50	60	1.0 M	90°C	60
SWa-M3-2	TMA	1.00	2	0.1 M	25°C	60
SWa-M3-60	TMA	1.00	60	1.0 M	90°C	60
SWa-L1	DDTMA	0.25	None	-----	-----	-----
SWa-L2	DDTMA	0.50	None	-----	-----	-----
SWa-L3	DDTMA	1.00	None	-----	-----	-----
SWa-L1-2	DDTMA	0.25	2	0.1 M	25°C	60
SWa-L1-60	DDTMA	0.25	60	1.0 M	90°C	60
SWa-L2-2	DDTMA	0.50	2	0.1 M	25°C	60
SWa-L2-60	DDTMA	0.50	60	1.0 M	90°C	60
SWa-L3-2	DDTMA	1.00	2	0.1 M	25°C	60
SWa-L3-60	DDTMA	1.00	60	1.0 M	90°C	60
SWa-O1	ODTMA	0.25	None	-----	-----	-----
SWa-O2	ODTMA	0.50	None	-----	-----	-----
SWa-O3	ODTMA	1.00	None	-----	-----	-----
SWa-O1-2	ODTMA	0.25	2	0.1 M	25°C	60
SWa-O1-60	ODTMA	0.25	60	1.0 M	90°C	60
SWa-O2-2	ODTMA	0.50	2	0.1 M	25°C	60
SWa-O2-60	ODTMA	0.50	60	1.0 M	90°C	60
SWa-O3-2	ODTMA	1.00	2	0.1 M	25°C	60
SWa-O3-60	ODTMA	1.00	60	1.0 M	90°C	60

TMA = Tetramethylammonium

DDTMA = Dodecyltrimethylammonium

ODTMA = Octadecyltrimethylammonium

Table 9. Showing the extents of organic cation exchange and acid treatments for Nontronite (SWa-1) derived samples.

Code	Organic cation (OC)	mg OC / g clay*	Clay acid treated (g)	Volume HCl (ml)	HCl Concn	Reaction Temp.	Acid contact time (minutes)
SAz-0	None	-----		-----	-----	-----	-----
SAz-30L	None	-----	1.0	100	6.0 M	25°C	30
SAz-90L	None	-----	1.0	100	6.0 M	25°C	90
SAz-180L	None	-----	1.0	100	6.0 M	25°C	180
SAz-30H	None	-----	1.0	100	6.0 M	90°C	30
SAz-90H	None	-----	1.0	100	6.0 M	90°C	90
SAz-180H	None	-----	1.0	100	6.0 M	90°C	180
SAz-32-30H	MAG	32	1.0	100	6.0 M	90°C	30
SAz-32-90H	MAG	32	1.0	100	6.0 M	90°C	90
SAz-32-180H	MAG	32	1.0	100	6.0 M	90°C	180
SAz-108-30H	MAG	108	1.0	100	6.0 M	90°C	30
SAz-108-90H	MAG	108	1.0	100	6.0 M	90°C	90
SAz-108-180H	MAG	108	1.0	100	6.0 M	90°C	180
SAz-173-30H	MAG	173	1.0	100	6.0 M	90°C	30
SAz-173-90H	MAG	173	1.0	100	6.0 M	90°C	90
SAz-173-180H	MAG	173	1.0	100	6.0 M	90°C	180

TMA = Tetramethylammonium

MAG = Magnafloc 206

*As found by TG Analysis

Table 10. Showing the extents of organic cation exchange and acid treatments for SAz-1 derived samples.

Code	Organic cation (OC)	mg OC / g clay*	Clay acid treated (g)	Volume HCl (ml)	HCl Concn	Reaction Temp.	Acid contact time (minutes)
SWy-0	None	-----		-----	-----	-----	-----
SWy-30L	None	-----	1.0	100	6.0 M	25°C	30
SWy-90L	None	-----	1.0	100	6.0 M	25°C	90
SWy-180L	None	-----	1.0	100	6.0 M	25°C	180
SWy-30H	None	-----	1.0	100	6.0 M	90°C	30
SWy-90H	None	-----	1.0	100	6.0 M	90°C	90
SWy-180H	None	-----	1.0	100	6.0 M	90°C	180
SWy-17-30H	MAG	17	1.0	100	6.0 M	90°C	30
SWy-17-90H	MAG	17	1.0	100	6.0 M	90°C	90
SWy-17-180H	MAG	17	1.0	100	6.0 M	90°C	180
SWy-128-30H	MAG	128	1.0	100	6.0 M	90°C	30
SWy-128 - 90H	MAG	128	1.0	100	6.0 M	90°C	90
SWy-128 - 180H	MAG	128	1.0	100	6.0 M	90°C	180
SWy-135-30H	MAG	135	1.0	100	6.0 M	90°C	30
SWy-135-90H	MAG	135	1.0	100	6.0 M	90°C	90
SWy-135 - 180H	MAG	135	1.0	100	6.0 M	90°C	180

TMA = Tetramethylammonium

MAG = Magnafloc 206

*As found by TG Analysis

Table 11. Showing the extents of organic cation exchange and acid treatments for SWy-2 derived samples.

HCl at 25°C for 60 minutes, (3) SWa-O3-60 is Nontronite which has been exchanged with 1.00 mmol octadecyltrimethylammonium cations/g clay then acid activated in 60 ml 1.0 M HCl at 95°C for 60 minutes, (4) SAz-M3-90L is SAz-1 which has been fully exchanged with tetramethylammonium cations, then acid activated in 100 ml 6.0 M HCl at 25°C (L for low temperature) for 90 minutes, (5) SWy-135-180H is SWy-1 which has been exchanged with 135 mg Magnafloc 206/g clay then acid activated in 100 ml 6.0 M HCl at 90°C (H for high temperature) for 180 minutes.

In order to establish the relative affinities of TMA^+ and H^+ for the clay surface a series of 'competitive' experiments were performed whereby a fixed concentration of TMA^+ solution (of constant volume) was added to the dried clay (1.5 g) at the same time as the required concentration of HCl. The total solution volume was constant. The concentration of TMA^+ solution was tailored to each particular clay of interest and was equal to 1 CEC, i.e. 1.2 mmol/g SAz-1 and 0.86mmol/g SWy-2. The acid concentration was also controlled so as not to exceed the CEC of the clay. The competitive exchange took place in low density polyethylene bottles oscillated at 280 r.p.m. at 28°C in a New Brunswick gyrotary water bath shaker for 18 hours. After exchange the clays were gravity filtered and washed with 25 ml deionised water. After centrifuging for 20 minutes at 20,000 r.p.m. the supernatant was decanted and the clay resuspended in 25 ml deionised water to remove any residual acid. The clay was centrifuged once more then air dried, ground and stored.

4.6.1 Techniques Used to Study the Effects of Acid Treatment.

XRF analysis and TG analysis were employed as discussed above (Sections 4.4.1 and

4.4.4 respectively), to study the effect of acid treatment both on the clay itself and on the resultant level of organic species present. Infrared spectroscopy was also employed.

Infrared spectroscopy performed by the author employed a ATI Mattson, Genesis Series Fourier Transform Infrared (FTIR) spectrometer. Infrared spectroscopy performed by co-workers employed a Nicolet Magna 750 Fourier Transform Infrared (FTIR) spectrometer. All spectra consisted of 256 scans at a resolution of 4 cm^{-1} . FTIR spectra of pressed KBr disks were obtained using standard procedures.

4.7 THE CATALYTIC REACTION.

All glassware was thoroughly dried before use. 50 mg catalyst was dried at 120°C overnight (16 hours). Samples dried for only 2 hours were also examined to determine that the longer drying time had not denatured the catalyst.

0.06 Moles of α -pinene (8.174 g) were weighed into a round bottom flask which was heated to the reaction temperature (80°C) by a hotplate and sand bath to ensure an even temperature distribution. A reflux condenser was attached although the reaction was not under reflux. The catalyst was taken to the reaction vessel in a dessicator to prevent rehydration. The catalyst was added to the pre-heated α -pinene and the flask was immediately swirled to aid mixing. After precisely 2 hours, the reaction mixture was poured into a syringe with a $0.2\text{ }\mu\text{m}$ syringe filter attached and expelled into a vial, thereby removing the catalyst. Control experiments indicated that the syringe filter did not retain any of the products and also that there was no further reaction after 5 days.

4.7.1 Techniques for Measurement of Catalytic Activity and Product Identification.

4.7.1.1 Gas Chromatography.

The filtered reaction mixture was analysed on a Perkin Elmer 8310B Gas Chromatograph with a 3% OV-225 chrom., WHP 80/100 mesh, 6' x 1/8" column fitted.

The conditions employed are given in Table 12.

Oven temperature	70°C
Isothermal	10 minutes
Injector temperature	150°C
Detector temperature	150°C
Hydrogen pressure	20 psi
Air pressure	30 psi
Nitrogen flow	12 ml/min

Table 12. Conditions employed for GC analysis of the catalysis of α -pinene.

4.7.1.2 Reproducibility of the Measurement of Catalytic Activity.

Reproducibility studies have been carried out by performing the catalytic reaction and measuring the % yields of camphene and limonene on at least two separate occasions for all polymer containing catalysts and a selection of tetraalkylammonium containing catalysts. Hence, the values quoted for % yield are $\pm 2\%$.

4.7.1.3 Gas Chromatography - Mass Spectrometry.

The products of the catalytic reaction were identified by gas chromatography coupled with mass spectrometry (GC-MS). The system used was a Unicam Automass System, benchtop quadropole mass spectrometer with an electron impact (EI) detector. The

column was a 30 m, 0.25 mm internal diameter, DB-1 (dimethylpolysiloxane). Details of the conditions employed are given in Table 13.

Splitless injection	10 seconds
Isothermal at 50°C	10 minutes
Gradient up to 225°C	35°C/minute
Isothermal at 225°C	10 minutes
Interface temperature	250°C
Source temperature	130°C
Ionisation energy	70 eV
Detector gain	700 volts
Mass range scan	4-200

Table 13. Conditions employed for identification of the catalysis products.

4.8 SAFETY PRECAUTIONS FOR EXPERIMENTAL PROCEDURES.

All procedures were carried out according to COSHH requirements. Exceptional care was required during the digestion and analysis of samples for Kjeldahl nitrogen analysis as highly concentrated acids and bases were used.

CHAPTER 5

Investigations into the Adsorption of Cationic Species By Clays.

5. INTRODUCTION.

Experiments were performed to determine how

- The type of clay,
- Clay purification,
- The nature of the exchange cation,
- Particle size,
- Ionic strength,

individually affect the adsorption of (poly)cations.

XRF analysis provided elemental analysis of the clay and several different analytical techniques were used to investigate the interactions of the (poly)cations with the clay surface namely:

- Kjeldahl nitrogen analysis,
- X-Ray Diffraction,
- Thermogravimetric Analysis.

5.1 XRF DETERMINATION OF THE ELEMENTAL COMPOSITION OF THE CLAYS INVESTIGATED.

XRF analysis provided elemental analysis of the clay and the oxides of the major elements are listed in Table 14.

The results also confirm the respective Na^+ and Cs^+ exchange of WL. Na_2O is present in WL as 0.2 % but in Na-WL this rises to 2.67 %. Similarly, there is no CsO present in WL but in the exchanged form this rises to 13.23 %.

Oxide	WL	Na-WL	Cs-WL	WL3	SWy-1	SWy-2	SAz-1	SHCa-1	SapCa-1
SiO ₂	76.10	75.84	66.18	77.06	68.04	68.48	67.72	45.94	61.40
Al ₂ O ₃	16.74	17.56	16.73	15.83	20.81	20.16	19.74	0.91	5.29
MgO	3.83	2.85	2.86	3.58	2.75	2.77	7.24	20.25	28.21
Fe ₂ O ₃	0.79	0.77	0.59	0.98	4.17	4.63	1.59	0.04	1.36
TiO ₂	0.33	0.23	0.24	0.24	0.12	0.09	0.27	0.06	0.66
CaO	1.89	0.03	0.04	1.93	1.87	1.76	3.16	30.97	1.50
Na ₂ O	0.21	2.67	0.07	0.23	1.65	1.70	0.07	1.66	1.37
K ₂ O	0.11	0.05	0.06	0.15	0.59	0.41	0.21	0.17	0.21
CsO	0.00	0.00	13.23	0.00	0.00	0.00	0.00	0.00	0.00
Total	100	100	100	100	100	100	100	100	100

Table 14. XRF data showing the elemental composition of the natural clays and two exchanged forms (Na-WL and Cs-WL). Only the major oxides are shown. Values are as % total weight.

The high CaO value obtained for SHCa-1 (30.97%), is due to the high level of calcium carbonate impurity in the natural clay.

5.2 ORGANOCATION ADSORPTION.

5.2.1 Kjeldahl Analysis of the Organoclay Complexes.

Clays were contacted with the cationic polymer and TMA⁺ and the resultant nitrogen content of the organoclay complex was determined by Kjeldahl analysis. The natural nitrogen content of the clays has been taken into consideration when calculating the (poly)cation uptake.

Table 15 shows the weight of (poly)cation (Magnafloc 206, [Me₂NCH₂CHOHCH₂]_n⁺, Figure 18a), and TMA⁺ (Figure 18c), required to fulfil the CEC if all the cation exchange sites on the clay surface were satisfied by cationic units on the (poly)cation.

Clay	CEC meq/100g	Magnafloc 206 required to fulfil the CEC (mg/g clay)	TMA ⁺ required to fulfil the CEC (mg/g clay)
WL	81	83	61
WL3	76	78	58
SWy-1	87	89	66
SWy-2	87	89	66
SAz-1	120	122	90
SHCa-1	80	82	61
SapCa-1	92	94	70

Table 15. Showing the weight of Magnafloc 206 and TMA⁺ required to fulfil the CEC.

SWy-2 shows similar adsorption properties and hence similar uptake curves to SWy-1.

Similarly, WL3 shows similar adsorption properties and hence similar uptake curves to WL, hence for clarity these curves are not shown in some figures relating to (poly)cation adsorption.

Figure 19 shows the uptake curves for Magnafloc 206 and TMA⁺ by WL, SWy-1 and SAz-1. The initial steep rise in the curves, where almost all the polycation offered is adsorbed, shows the strong affinity of the polycations for the clay surface. Conversely, the uptake curves for adsorption of TMA⁺, which represents the cationic portion of the polymer, show a weaker affinity for the clay compared to the polymer as shown by the shallower initial rise than in the polymer adsorption isotherms. Also, the plateau reached for polymer adsorption for each type of clay is higher than the plateau reached for TMA⁺ uptake. This shows that each clay adsorbs more organic species as Magnafloc 206 than TMA⁺. Of the samples shown in this Figure, the highest affinity of (poly)cations for the clay surface is exhibited by the polymer for SWy-1, as shown by the steeper initial rise in the uptake curve.

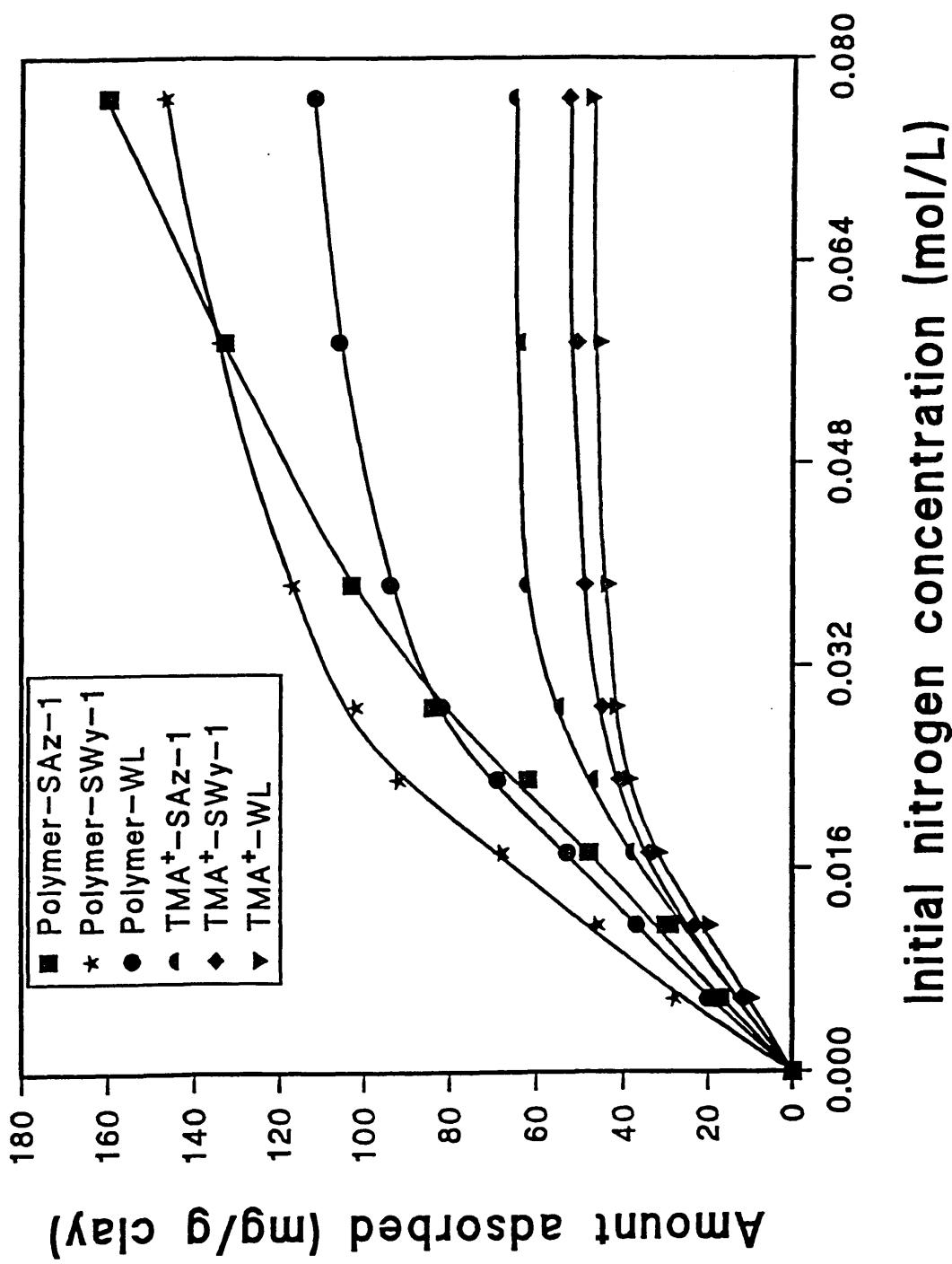


Figure 19. Showing the uptake curves of Magnafloc 206 and TMA⁺ by WL, SWy-1 and SAz-1

Figure 20 shows the adsorption isotherms for TMA^+ , by the unsedimented heterionic clays. In all cases the initial rise of the uptake curves is shallow indicating that the affinity of the TMA^+ cations for the clay surface is not strong. At an initial nitrogen concentration of 80 mmole/L (the maximum studied in this work), Q_{\max} was 65 mg/g for SAz-1 (72% CEC), 58 mg/g for SapCa-1 (83% CEC), 53 mg/g for SWy-1 (80% CEC), 48 mg/g for WL (78% CEC), 31 mg/g for SHCa-1 (51% CEC). The uptake reflects the CEC of the clays (see Table 15), and also the degree of dispersion, i.e. uptake decreases in the order SAz-1 > SapCa-1 > SWy-1 > WL > WL3. The uptake on SHCa-1 is relatively low as a result of the high calcite content of the clay (XRF shows that $\text{CaO} = 30.97\%$, see Table 14), which is non-adsorbing.

Figure 21 compares polycation (MagnaFloc 206) adsorption on the unsedimented, heterionic forms of the different types of clay. All of the isotherms indicate that the polycations have a high affinity for the clay surface as shown by the initial steep rise in the curve. This then reaches a plateau at high polymer adsorption where the amount adsorbed does not increase significantly. The initial rise of the polymer uptake curve for all clays investigated is steeper than for the corresponding TMA^+ uptake curve which shows that the polycations have a higher affinity for the clay surfaces than TMA^+ cations. The amount of MagnaFloc 206 adsorbed exceeds the CEC by 38 mg/g for SAz-1 (131% CEC, but still rising), 41 mg/g for SapCa-1 (144% CEC), 58 mg/g for SWy-1 (165% CEC), 29 mg/g for WL (135% CEC) and 8 mg/g for SHCa-1 (110% CEC). SHCa-1 shows a rapid initial adsorption but a low plateau value compared to the other clays analysed. The low plateau is again due to the high calcite content of the clay. SAz-1 and SWy-1 show a less steep initial uptake and do not reach a plateau. The amount adsorbed continues to rise with the increase in initial nitrogen concentration.

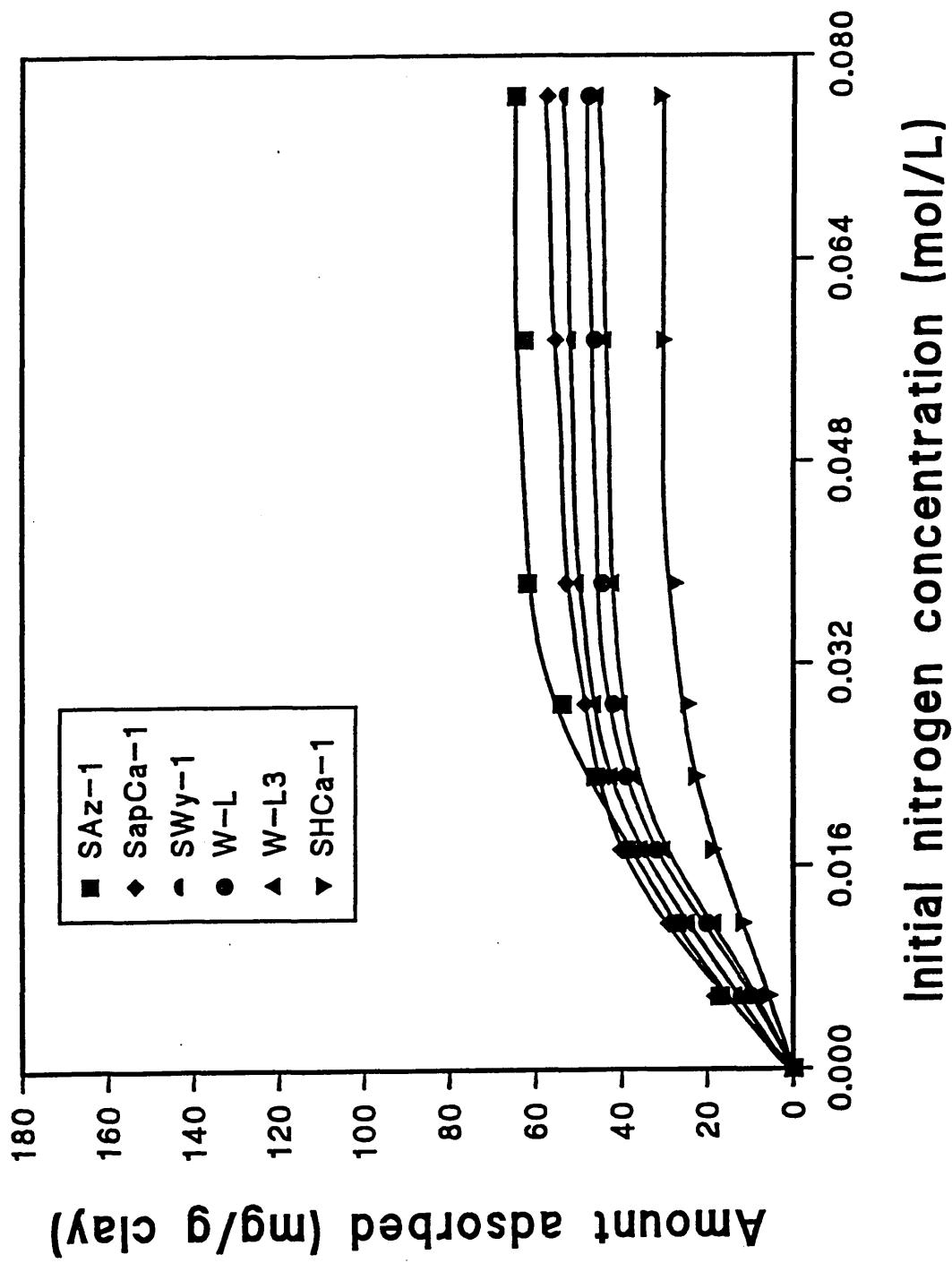


Figure 20. Showing the uptake curves for TMA^+ by the unsedimented, heterionic clays.

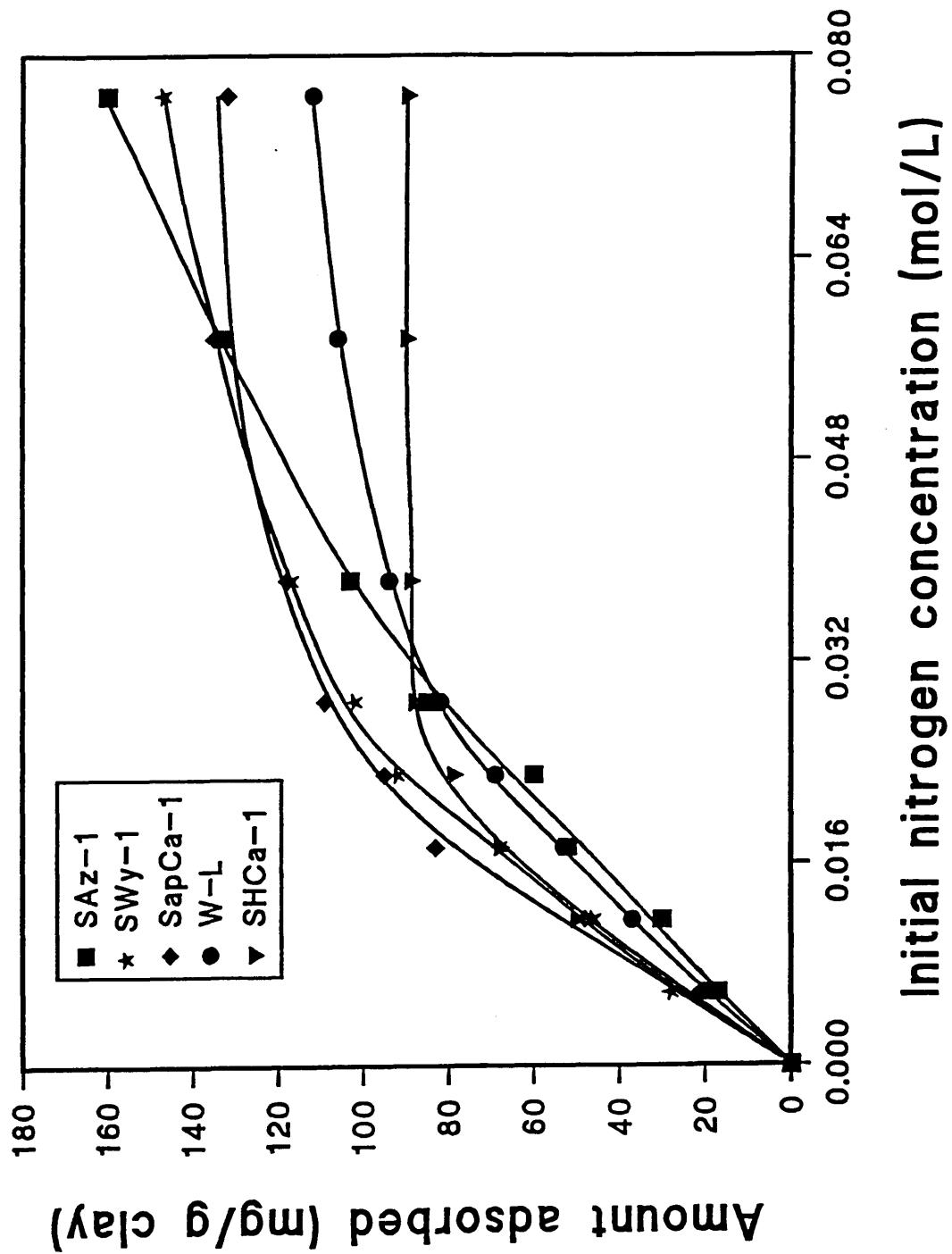


Figure 21. Showing the uptake curves for Magnafloc 206 by the unsedimented, heterionic clays.

Q_{\max} for Magnafloc 206 on WL is 110 mg/g (Figure 21) compared to 48 mg/g for TMA⁺ on WL (Figure 20) and a similar difference in uptake is noted for SAz-1 (160 mg/g compared to 65 mg/g) and SapCa-1 (135 mg/g compared to 58 mg/g). TMA⁺ cations are good at replacing ions from the clay as a result of their low hydration energy, but have a lower affinity for the clay compared to Magnafloc 206 as shown by the shallower initial rise in the curves. This is in agreement with Breen *et al.*¹⁸⁵ who studied the adsorption of polymers with the same structure ($[\text{Me}_2\text{NCH}_2\text{CHOHCH}_2]_n^{n+}$), but different molecular weights (5,000 and 100,000), and TMA⁺ on montmorillonite. They also found that TMA⁺ was moderately effective (with paraquat²⁺ being more effective and Na⁺ and K⁺ ions ineffective) at displacing resident Cs⁺ ions from the clay.

The point of zero charge (PZC) should be reached when the number of cationic units absorbed matches the anionic centres on the clay. Build up of charge detected on the polymer/clay particles before the CEC is reached may indicate (i) inefficient displacement of the exchange cations, or (ii) the presence of a significant number of loops or trains which are not in contact with the clay surface. Since cationic polymers are generally adsorbed via the instantaneous collapse of the polycation chain onto the surface of the clay, resulting in a large number of train segments and relatively few short loops¹⁶⁵, (i) is more likely. The positively charged polyammonium cation exchanges into the clay interlayer and displaces sodium ions. The multiple cationic sites that are connected together enable the polymer to bind the clay particles together effectively.

As part of their studies, Breen *et al.*¹⁸⁵ made zeta potential and particle size measurements on the polymer/Cs-montmorillonite interactions. They found that the PZC and the minimum of the particle-size curve for the adsorption of polymer on Cs-

montmorillonite indicated that the negative charge on the particles was equalised at 60% CEC. After this, further adsorption of polymer resulted in a build up of positive charge and re-establishment of electrostatic stabilisation. Also, upon further polymer addition displacement of Cs^+ continued. Breen *et al.*¹⁸⁵ concluded that the polymer was adsorbed via a charge neutralisation process which led to flocculation via the electrostatic patch model (Section 3.11.1). A simple bridging mechanism was not thought possible since the polymers they studied did not have very long chain lengths compared to the size of the clay platelets.

Figure 22 shows the uptake of PAA, (poly(allylamine hydrochloride), Figure 18b), and Magnafloc 206 on WL. The initial rise of the uptake curve for PAA was more shallow than that for Magnafloc 206, showing that PAA has a lower affinity for the clay surface. Over the range of initial nitrogen concentrations studied, Q_{\max} for PAA uptake (100 mg/g) was lower than for Magnafloc 206 uptake (112 mg/g), although both uptake curves are still rising.

The distance between two exchange sites on the clay is about 11 \AA^{180} . In Magnafloc 206 (Figure 18a), the distance between cationic centres is approximately 5.5 \AA which equals half the distance between anionic sites on the clay. Consequently, alternate N groups on the polycation are a good match for the clay resulting in a strong affinity⁸⁰. Since only half the cationic sites on the polymer will be satisfied by the clay, some, or all of, the remaining charge must be satisfied by a counter ion. The counter ion for the polymer is Cl^- and it is thought that this is accommodated somewhere in the clay-polymer complex, probably in close proximity to unsatisfied cationic sites on the polymer.

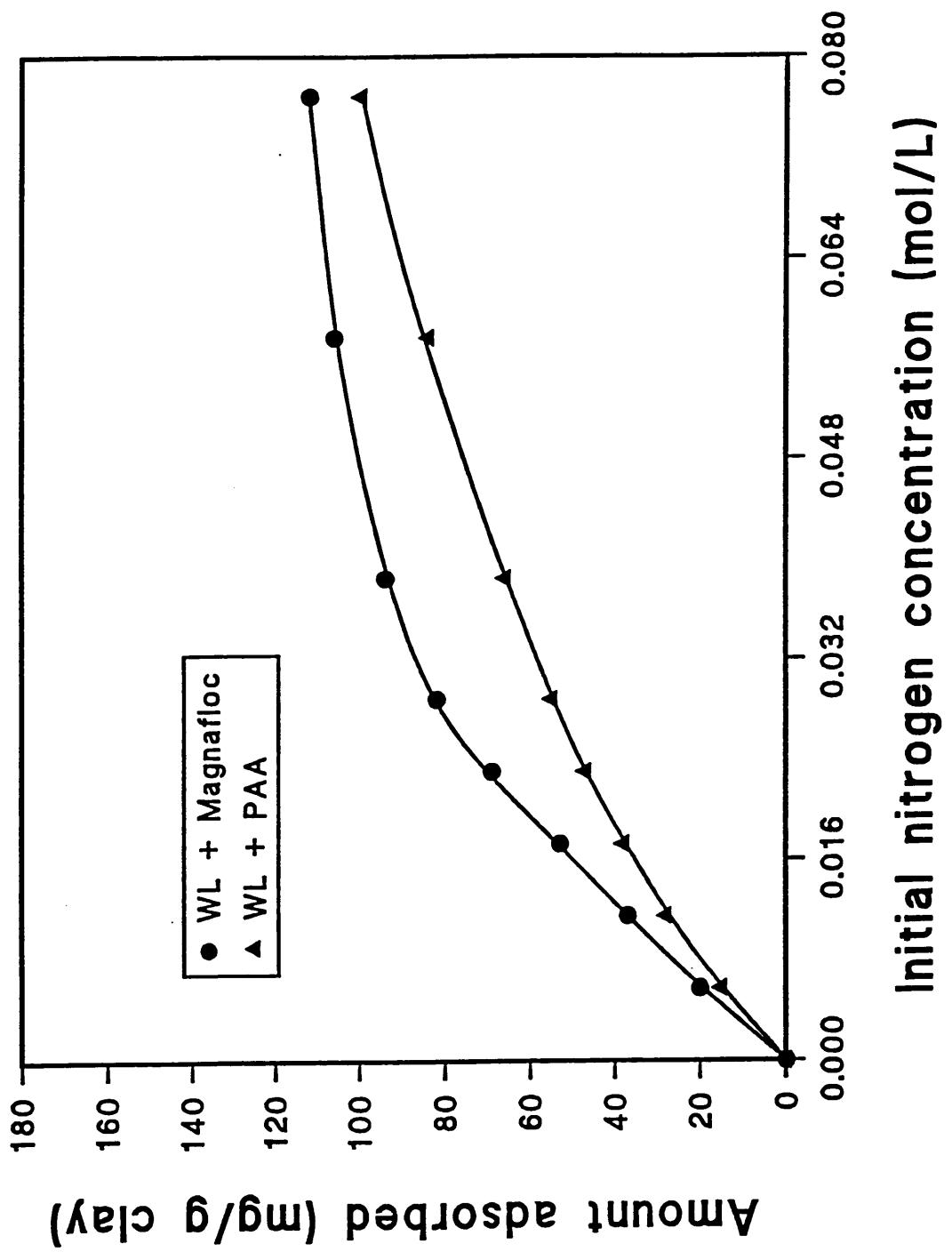


Figure 22. Showing the uptake of PAA and Magnafloc 206 on WL.

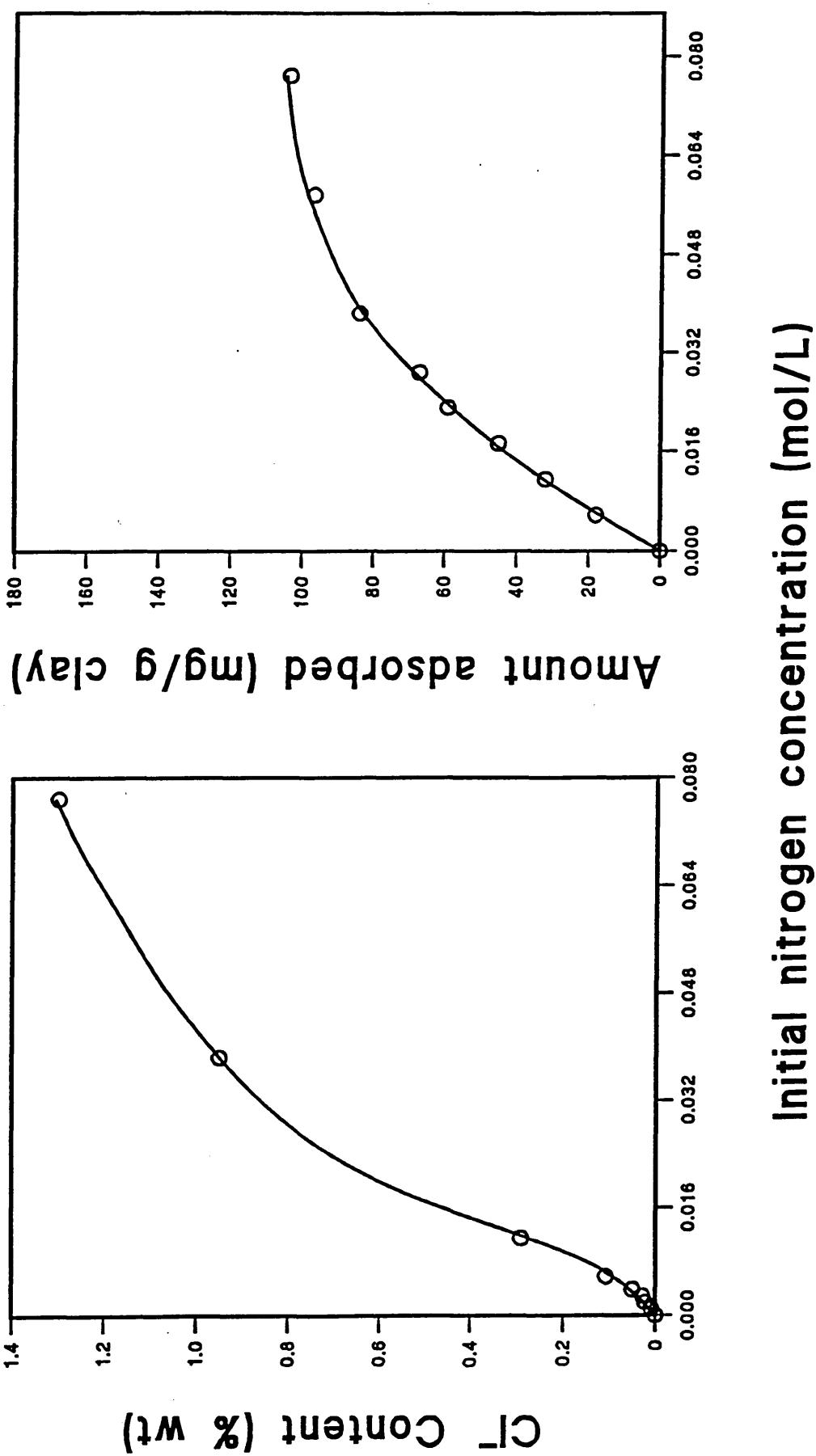


Figure 23. Comparing (a) the amount of chloride present, with (b) the corresponding adsorption isotherm for Magnafloc 206 on unsedimented, heterionic WL3.

Figure 23a compares the amount of chloride present, determined using semi-quantitative x-ray fluorescence (XRF) analysis of pressed powder samples, with the corresponding adsorption isotherm for Magnafloc 206 on unsedimented, heterionic WL3 shown in Figure 23b. Pressed powder samples (which only gave semi-quantitative results because the spectrometer was not fully calibrated for pressed powders), must be used for XRF analysis in this case as Cl^- is too volatile for the fusion of beads and is lost in the exhaust fumes from the furnace. It can be seen that there is a significant increase in chloride content with the sorbed amount of polymer, confirming the presence of some counterions in the clay-polymer complex.

Sorption by clay minerals is the sum of interlamellar uptake and uptake on external surfaces. The adsorption isotherms are characterised by an initial steep rise followed by a plateau indicating little further adsorption. The initial steep rise is mainly due to ion exchange adsorption and the plateau region is characteristic of molecular adsorption. However, Figure 23 shows that adsorption of Cl^- ions occurs to a small extent at low loadings of polymer and increases to show a steeper isotherm compared to polymer adsorption. This suggests that to an extent, the two mechanisms of molecular and ion exchange adsorption must be occurring simultaneously. It also suggests that at higher loadings of polymer some of the Cl^- counter ions must be retained and this may give the clay some anion exchange capacity. This is in agreement with the findings of Ueda and Harada¹⁸² who investigated the adsorption of cationic polysulfone (diallyldimethylammonium chloride - SO_2 copolymer, molecular weight 16.7×10^4), on Na-montmorillonite and found that the clay developed some anion exchange capacity as a result of the excess adsorption of the polycation. As the amount of copolymer

adsorbed increased from 0 to 14.5 mg/g, the anion exchange capacity increased from 0 to 18.2 meq/100g.

Figure 24 shows the influence of particle size and the exchange cation on Magnafloc 206 uptake. It compares the amount of polymer adsorbed on unsedimented, heterionic WL with unsedimented Na-WL, size fractionated (sedimented) heterionic WL, size-fractionated (sedimented) Na-WL and size-fractionated (sedimented) Cs-WL. Q_{\max} for unsedimented Na-WL (125 mg/g), is greater than that for unsedimented heterionic WL (106 mg/g). Q_{\max} for Cs-WL (114 mg/g), is significantly lower than for any of the Na-exchanged samples. This is explained in terms of the nature of the suspension of the clays. As discussed in Section 2.5, Norrish⁵⁷ showed that the layers in Na-montmorillonite could be expanded stepwise with the addition of water layers to anhydrous Na-montmorillonite at 9.6 Å to give a basal spacing of 40 Å, above which the layers are taken to be completely dissociated. Hence, Na-montmorillonite gives rise to a peptised suspension. When the exchange sites are occupied by ions other than Na^+ , e.g. Ca^{2+} , the clay platelets tend to aggregate and form tactoids more readily thus reducing the available basal surface of the clay²⁸². The results shown in Figure 24 are in agreement with the findings of Schamp and Huylebroeck¹⁷⁰ who investigated the adsorption of neutral polymers onto clays. They found that the amount of neutral polymer adsorbed was many times higher on the peptised sodium exchanged montmorillonite than on the aggregated and flocculated hydrogen exchanged montmorillonite.

Gu and Doner¹⁸³ made similar observations when they investigated the adsorption of cationic polysaccharide (PSS) by illite saturated with different cations at about neutral

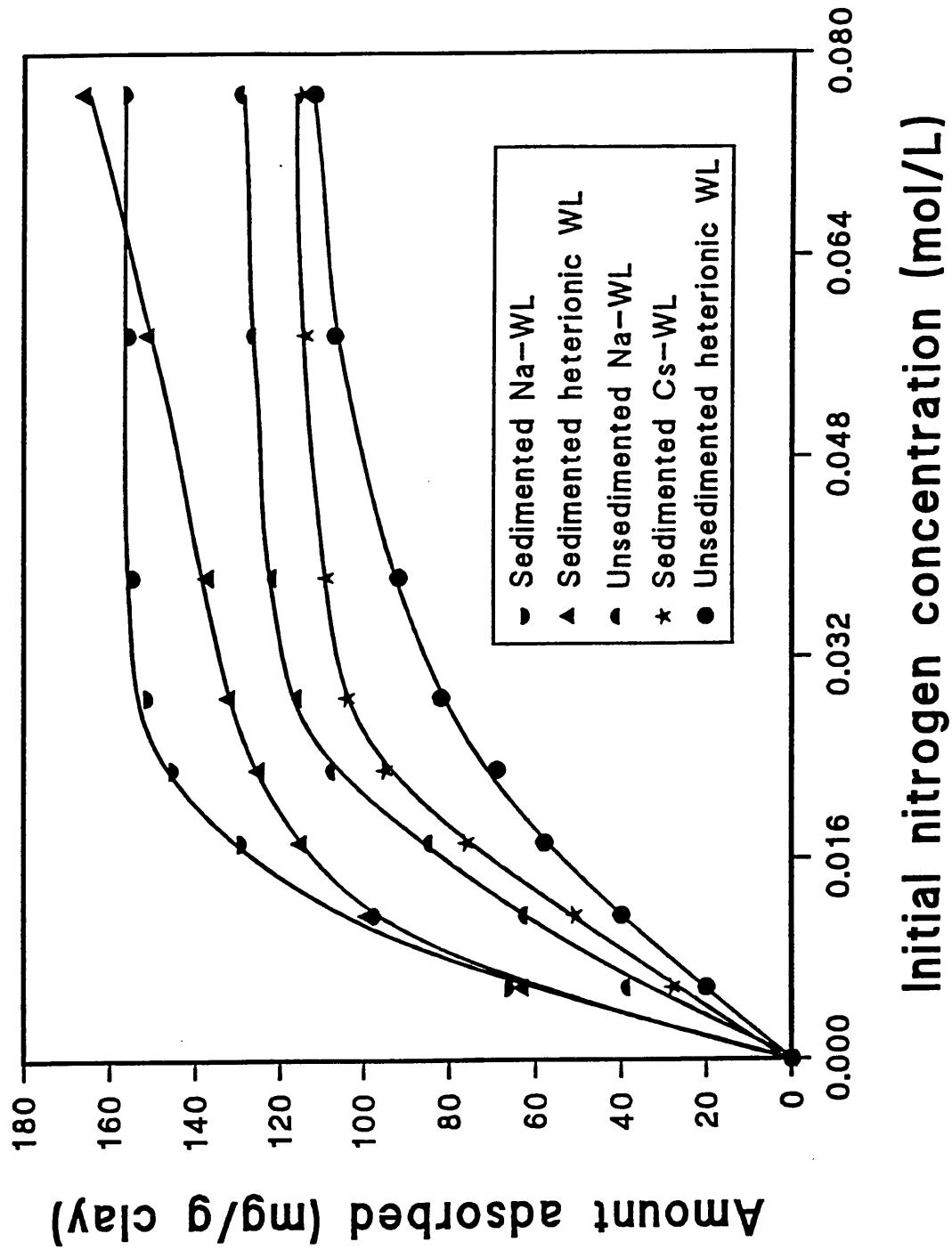


Figure 24. Showing the influence of particle size and exchange cation on Magnafloc 206 uptake.

pH. They noted that PSS exhibited a very high affinity for the clay surface and that Q_{\max} for Na-illite was greater than for Ca-illite. Also, illite exchanged with hydroxy-Al polycations (Al-p, $10^4 < \text{molecular weight} < 5 \times 10^4$), resulted in a three-fold decrease in PSS adsorption compared with Na-illite. Na^+ resides mainly in the diffuse double layer and can be readily exchanged by other cations. Conversely, Al-p forms strong complexes with the clay surface and cannot be readily exchanged by other cations, especially monovalent cations¹⁸⁴. As a result, Al-p-illite forms large tactoids thus reducing accessibility of PSS to the clay surface. Hence Gu and Doner¹⁸³ also deduced that the order of PSS adsorption, Na-illite > Ca-illite > Al-p-illite, was related to tactoid size, Na-illite < Ca-illite < Al-p-illite, showing that accessibility to the clay surface was also significant.

Figure 24 also highlights the different affinities of the polymer for sedimented and unsedimented clay and also Na^+ and Cs^+ exchanged montmorillonite. Magnafloc 206 has a much higher affinity for sedimented WL compared to unsedimented WL as shown by the steeper initial rise of the uptake curves for the sedimented sample. The same effect is seen for sedimented Na-WL compared to unsedimented Na-WL. The removal of impurities from the clay clearly increases the affinity of the polymer for the clay surface and increases the value of Q_{\max} . Weight for weight there will be more clay present in the purified (sedimented) fraction than in the unpurified (unsedimented) fraction, as the latter will contain small quantities of silica and other non-adsorbing impurities. There is a similar affinity of the polymer for the clay surface following either sedimentation only or sedimentation and Na^+ exchange as shown by the similarly steep initial rise of the uptake curves which is much steeper than the other curves shown. Conversely, there is a relatively low Q_{\max} and affinity of the polymer for the surface of

sedimented Cs-WL as compared to sedimented Na-WL. This shows the effect that the exchangeable cation associated with the clay has on its ability to swell and the degree of platelet dispersion. Suspensions of Na-montmorillonite are predominantly deflocculated and consequently, the cationic polymer has access to the total surface area of the clay. With suspensions of Cs-montmorillonite the platelets are aggregated into tactoids and the swelling ability of this clay is minimal as compared to Na-montmorillonite. Consequently, due to the aggregation of platelets, this clay shows reduced Q_{\max} values for the uptake of polymer. This is in agreement with the findings of Breen *et al.*¹⁸⁵ who found that Q_{\max} for the adsorption of polymer ($[\text{Me}_2\text{NCH}_2\text{CHOHCH}_2]^{n+}$ of molecular weight 5,000 and 100,000), on Na-montmorillonite was much greater than on Cs-montmorillonite.

An additional feature of Figure 24 is the shape of the uptake curve onto heterionic WL (both unsedimented and sedimented) compared to that on Na-WL (and Cs-WL) samples. In the latter case the plateau region is well defined with no further adsorption occurring after an initial nitrogen concentration of 28 mmol/L. However, with the heterionic samples, further adsorption continues beyond that initial nitrogen concentration suggesting that molecular adsorption makes a greater contribution in the heterionic system, although impurities may also make a contribution.

Figure 25 compares Magnafloc 206 adsorption on sedimented Na-WL in non-saline and high saline (0.5 M NaCl) conditions and suggests that at low polymer concentrations, increasing the ionic strength of the medium decreases the total amount of polymer adsorbed. However, at initial nitrogen concentrations over 32 mmol/L, no more polymer is adsorbed by sedimented Na-WL in non-saline conditions, whereas adsorption

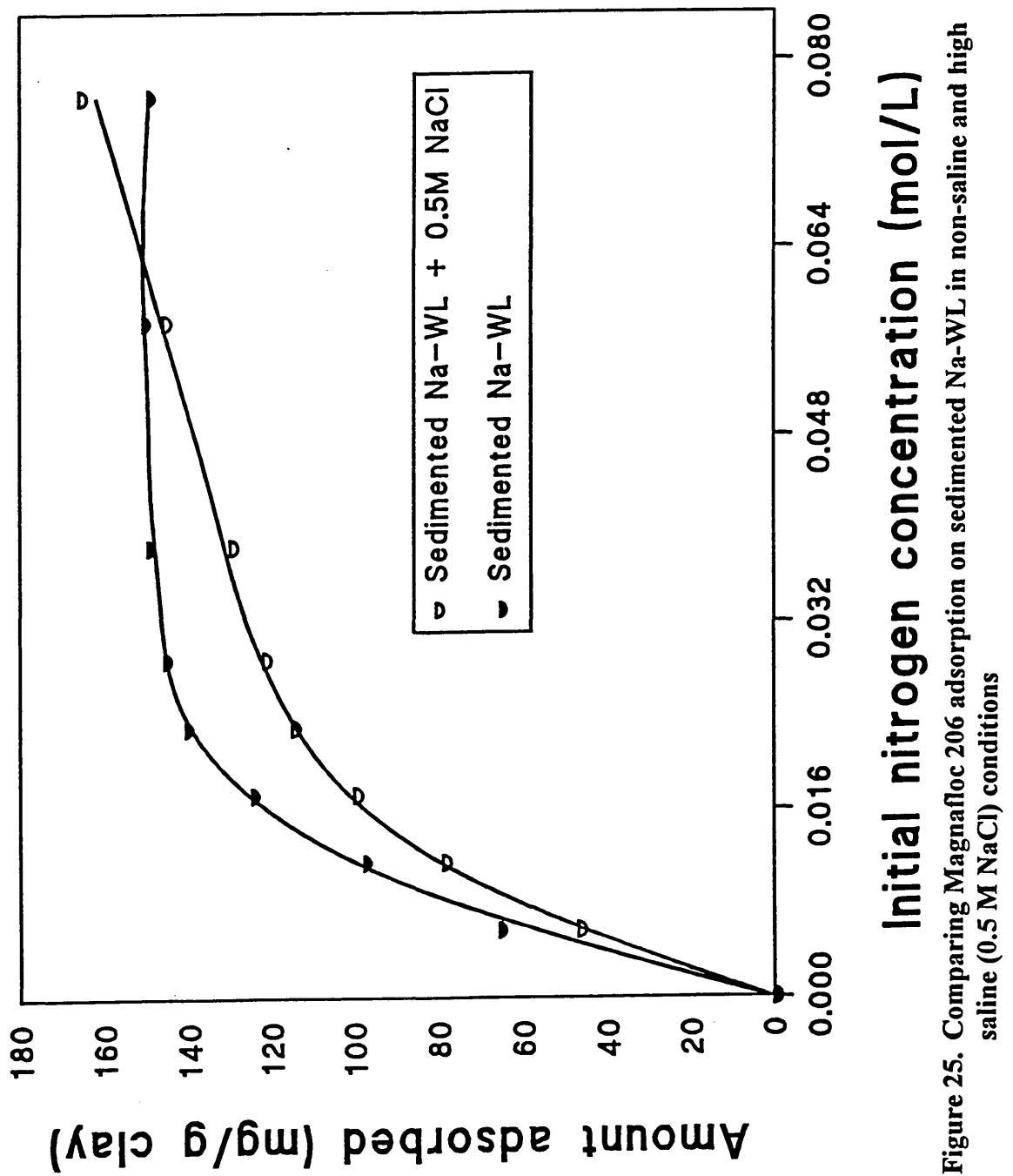


Figure 25. Comparing Magnafloc 206 adsorption on sedimented Na-WL in non-saline and high saline (0.5 M NaCl) conditions

continues in high saline conditions. At an initial nitrogen concentration of 80 mmole/L (the maximum studied in this work), Q_{\max} for sedimented Na-WL in non-saline conditions is 150 mg/g, whereas in high saline conditions Q_{\max} is 166 mg/g and still rising. These findings at lower initial nitrogen concentrations (< 60 mmol/L), agree in principle with Bailey *et al.*²⁸³ who found that as the ionic strength of the dispersion medium was increased there was a decrease in uptake for anionic polymer adsorption. The higher the electrolyte concentration the higher is the rate of clay flocculation and the lower the fraction of available surface area. This is primarily due to compression of the electrical diffuse double layer at the surface of the clay platelets which reduces the ability of the platelets to repel one another and hence, aggregation can occur (as discussed in Section 2.6). The competition between inorganic cations and the cationic polymers for adsorption sites on the negatively charged clays also increases with electrolyte concentration, leading to reduced polymer adsorption, but this is a much smaller effect.

At high initial nitrogen concentrations (> 60 mmol/L), the results shown in Figure 25 agree with those of Espinasse and Siffert¹⁷⁷ who studied the addition of partially hydrolysed polyacrylamide (PHPA, molecular weight (i) 6×10^6 and (ii) 11×10^6), onto Na-montmorillonite. They found that Q_{\max} increased from (i) 2.4 mg/g clay and (ii) 2.8 mg/g clay in conditions of low ionic strength (i.e. no added salt), to (i) 13 mg/g clay and (ii) 15 mg/g clay in conditions of high ionic strength (100 g/L NaCl). They suggest that the increase in ionic strength (salinity) has the effect of screening the negative charges on the polymer both from one another and from those associated with the clay platelets, thus allowing the polymer greater contact with the clay surface.

In addition to their work mentioned above on the effect of NaCl on the adsorption of cationic polysulfone on Na-montmorillonite, Ueda and Harada¹⁸² also investigated the effect on adsorption of the quantity of NaCl in the dispersion medium. As the ionic strength increased from 0 to 1.25 mol/L, the adsorption of the copolymer increased from 9.6 to 13.4 mg/g and the anion exchange capacity (AEC) of the complex increased from 5.0 to 21.4 meq/100g. They suggested that the polymer chain in NaCl solution exists in a coiled configuration and retains this configuration when it is adsorbed onto the clay surface. Hence, the cationic sites of the polymer cannot combine effectively with the anionic sites of the clay thus adsorption of the copolymer increases. This agrees with the findings presented herein (Figure 25), at high initial nitrogen concentrations (> 60 mmol/L).

5.2.2 XRD Analysis of Clays And Organoclay Complexes.

XRD can be used to establish the interlayer spacing of clays. By measuring the first order basal reflections (d_{001}) of the sample it is possible to establish whether the organic cations are adsorbed, (i) exclusively on the surface of the clay which would not affect the interlayer spacing; or (ii) whether some cations reside between the clay platelets, which would increase the natural spacing. Measurement of the 2θ value permits the calculation of the d_{001} spacing. However, many organic-expanded clay samples exhibit d_{001} spacings which are difficult to distinguish from water expanded spacings. It is often useful therefore, to investigate the thermal stability of the expanded clays to obtain a fuller picture.

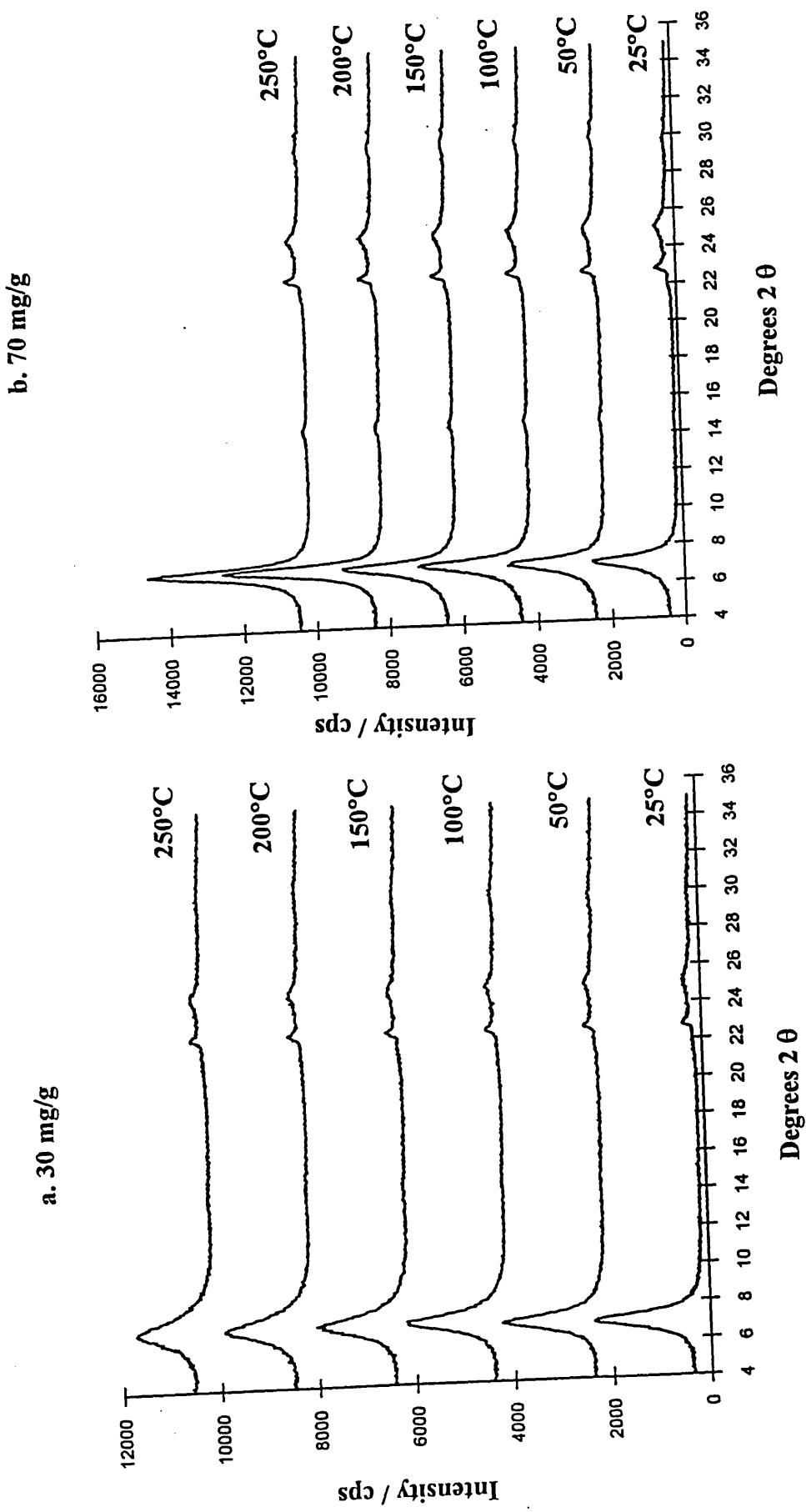


Figure 26. Showing the VT-XRD traces obtained for 2 loadings of TMA^+ on WL, a. 30 mg/g, b. 70 mg/g.

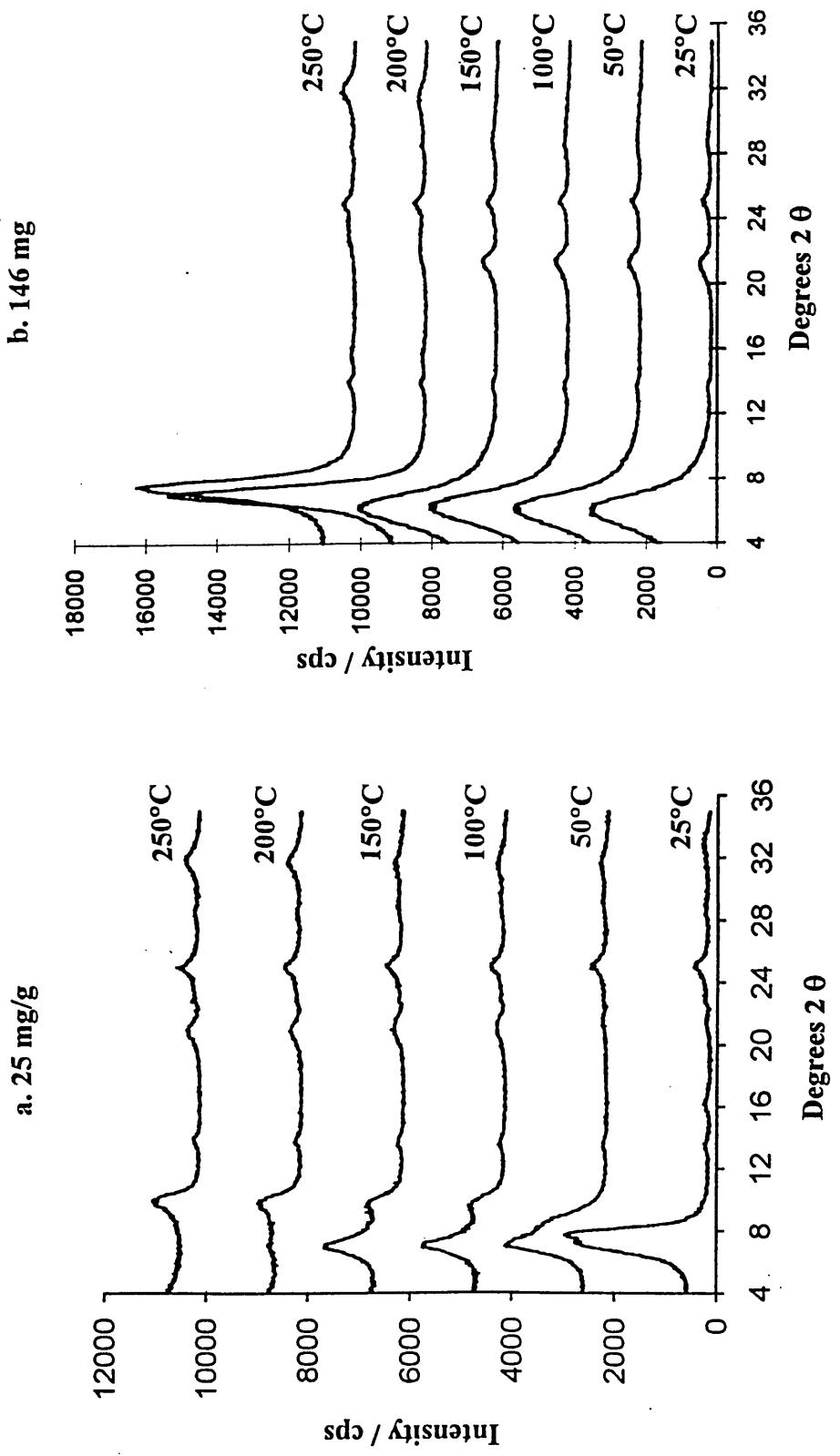


Figure 27. Showing the VT-XRD traces obtained for 2 loadings of Magnafloc 206 on Na-WL,
a. 25 mg/g, b. 146 mg.

Clay	Organocation	Mol L ⁻¹ N added	Amount adsorbed mg/g*	d ₀₀₁ Ambient /Å	d ₀₀₁ 50°C /Å	d ₀₀₁ 100°C /Å	d ₀₀₁ 150°C /Å	d ₀₀₁ 200°C /Å	d ₀₀₁ 250°C /Å
Na-WL	None	0	0	13.51	11.30	10.13	10.13	10.06	10.13
Na-WL	Polymer	1.92 × 10 ⁻³	25	13.08	14.33	14.45	14.45	10.25	10.13
Na-WL	Polymer	5.76 × 10 ⁻³	67	14.58	14.71	14.71	14.71	14.33	10.71
Na-WL	Polymer	9.60 × 10 ⁻³	81	14.84	14.71	14.71	14.71	14.45	13.29
Na-WL	Polymer	2.30 × 10 ⁻²	146	17.51	17.14	16.63	16.63	15.68	14.45
Na-WL	Polymer	5.76 × 10 ⁻²	156	16.97	16.63	16.46	16.46	14.45	13.51
WL	TMA ⁺	1.15 × 10 ⁻³	29	14.33	14.33	14.33	14.33	14.21	14.33
WL	TMA ⁺	5.76 × 10 ⁻²	68	14.33	14.33	14.21	14.33	14.20	14.33

* loadings obtained from TG analysis

Table 16. Showing the basal spacings for a selection of samples.

The quality of the diffraction data at different temperatures is given in Figures 26 and 27 and the basal spacings for a selection of samples are given in Table 16.

VT-XRD traces for WL exchanged with different loadings of TMA⁺ (a, 30 mg TMA⁺/g clay, 37% CEC, and b, 70 mg TMA⁺/g clay, 85% CEC), are shown in Figure 26. In each case, the TMA-WL complex is thermally stable up to 250°C as shown by the invariance of the peak at 14.08 Å ($2\theta = 7.28^\circ$). There are no obvious peaks due to the presence of water in the interlayer, suggesting that (i) the TMA⁺ cation is present within all layers (as the TMA⁺ cation is larger in size than a water molecule only the spacing due to the TMA⁺ cations will be observed); and (ii) the TMA⁺ cations are more thermally stable and can prop the layers apart even when the system is dehydrated, as first seen by Barrer and MacLeod⁹.

At low polymer loadings (e.g. 25 mg/g), the basal spacing at ambient temperature is similar to that obtained when one water layer is present (Table 16). However, upon initial heating at 50°C two separate spacings are apparent. Figure 27a shows the diffraction trace obtained for Na-WL loaded with 25 mg polymer/g clay (26% CEC). Two poorly resolved peaks around $2\theta = 8.2^\circ$ (corresponding to a basal spacing of 13 Å), were present at ambient temperature, the origin of which only becomes apparent after heating. $d_{001} = 12.6$ Å for non-organocation exchanged hydrated clay, and the poorly resolved initial peaks occur at basal spacings of 14.6 and 12.6 Å. After heating the sample at 50°C for 30 minutes, dehydration occurs causing the water-filled layers to collapse²⁸⁴. Conversely, the polymer-filled layers require a higher temperature to denature the polymer and cause layer collapse. Only the peak at 14.6 Å remains which corresponds to the thickness of one polycation layer between the sheets, thus confirming

that the polycation resides between the clay layers. Hence, below 50°C there must be polymer present in some layers and water present in others, resulting in the appearance of the two poorly resolved peaks. The peak at 14.6 Å is stable up to 150°C which is sufficient to denature the polymer, causing complete collapse of the clay layers, resulting in a spacing of 9.6 Å (see TG analysis results below, Section 5.2.3).

At higher loadings (e.g. 146 mg polymer/g clay, 153% CEC), the organoclay complex is more thermally stable and increased d_{001} spacings (Table 16), are observed, Figure 27b. The polymer was only slightly denatured at 200°C as shown by the decrease in spacing (higher value of 2θ), and collapse had not occurred by 250°C, the highest temperature available for these studies. There is also evidence of a peak at 16 Å ($2\theta = 6.3^\circ$), at temperatures < 200°C, which suggests that there is more than one polymer layer between the sheets. It is likely that this peak is the average of spacings due to one polymer layer (14.6 Å) and two polymer layers (19.6 Å). The broader peaks here suggest that the system is less well ordered.

These findings of the segregation of the adsorbed polymer into different interlayers at low loadings and the presence of more than one polymer layer between the aluminosilicate sheets at high loadings, agree with the findings of Breen *et al.*¹⁸⁵ who studied the adsorption of polymer ($[\text{Me}_2\text{NCH}_2\text{CHOHCH}_2]_n^+$, molecular weight 5,000 and 100,000) by Na-montmorillonite.

The change in basal spacing with adsorbed polyamine has also been studied by Billingham *et al.*²⁸⁵ who investigated the adsorption by Na-SWy-1 of a polymer with the same structure as that used by Breen *et al.*¹⁸⁵, and herein, but of molecular weight

5,000. Billingham *et al.*²⁸⁵ found that adsorption of the polymer onto Na-SWy-1 caused the basal spacing to increase from 12.9 Å to \geq 15.2 Å. Billingham *et al.* also immersed preformed films of Na-SWy-1 containing (i) low, and (ii) high loadings of polymer into polyethylene glycol (PEG, molecular weight 300) solutions. At low loadings of polymer, where the CEC was not fully satisfied, immersion of the preformed film into PEG caused an increase in basal spacing to 18.6 Å, which was attributed to the presence of two layers of PEG lying flat between clay lamellae where polycation was not present. Conversely, immersion of the preformed film containing high loadings of polymer did not increase the basal spacing from 15.2 Å, attributed to polymer exchanged Na-SWy-1. The strong attractive forces between the polymer and the clay sheets prevented the adsorbed PEG from separating the sheets and forming bilayers. This indicates the ‘swellability’ of SWy-1 montmorillonite with different loadings of polymer.

5.2.3 Thermogravimetric Analysis of Organoclay Complexes.

Thermogravimetric (TG) analysis was performed on organoclay complexes to confirm the thermal stability which had been indicated by VT-XRD data, and to compare weight loss data with the results obtained by Kjeldahl analysis for polymer loading.

Figure 28 illustrates the derivative thermograms observed for the increased loading of polymer on sedimented Na-WL. The peak at 90°C (peak a) is due to the loss of interlayer water associated with the clay which has all been removed by 150°C. As the amount of adsorbed polymer increases, so do the peaks at approximately 275 and 410°C, as expected. Hence, the region 160-520°C corresponds to the breakdown and loss of

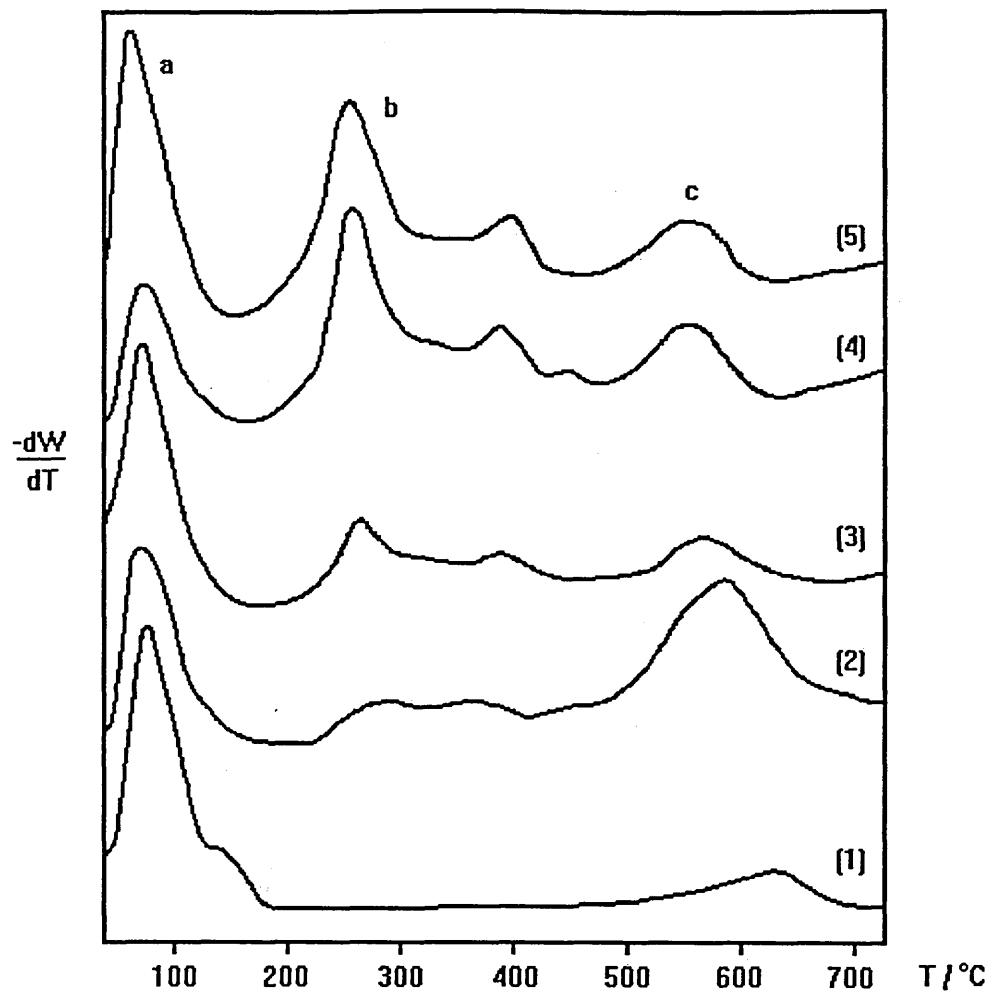


Figure 28. TGA traces recorded for increasing loadings of Magnafloc 206 on Na-WL. (1) 0 mg/g, (2) 66 mg/g, (3) 97 mg/g, (4) 150 mg/g, (5) 156 mg/g.

polymer, although the major loss occurs at around 275°C (peak b), as shown by the greater relative intensity of this peak. The broad peak observed between 590 and 680°C (peak c), is due to the loss of structural hydroxyl groups, as water, from the clay.

Figure 29 shows the amount of Magnafloc 206, as detected by Kjeldahl analysis, versus the % weight loss as determined by TG analysis, of polymer loaded Na-WL. The straight line observed suggests that thermal treatment of the polymer gives rise to the

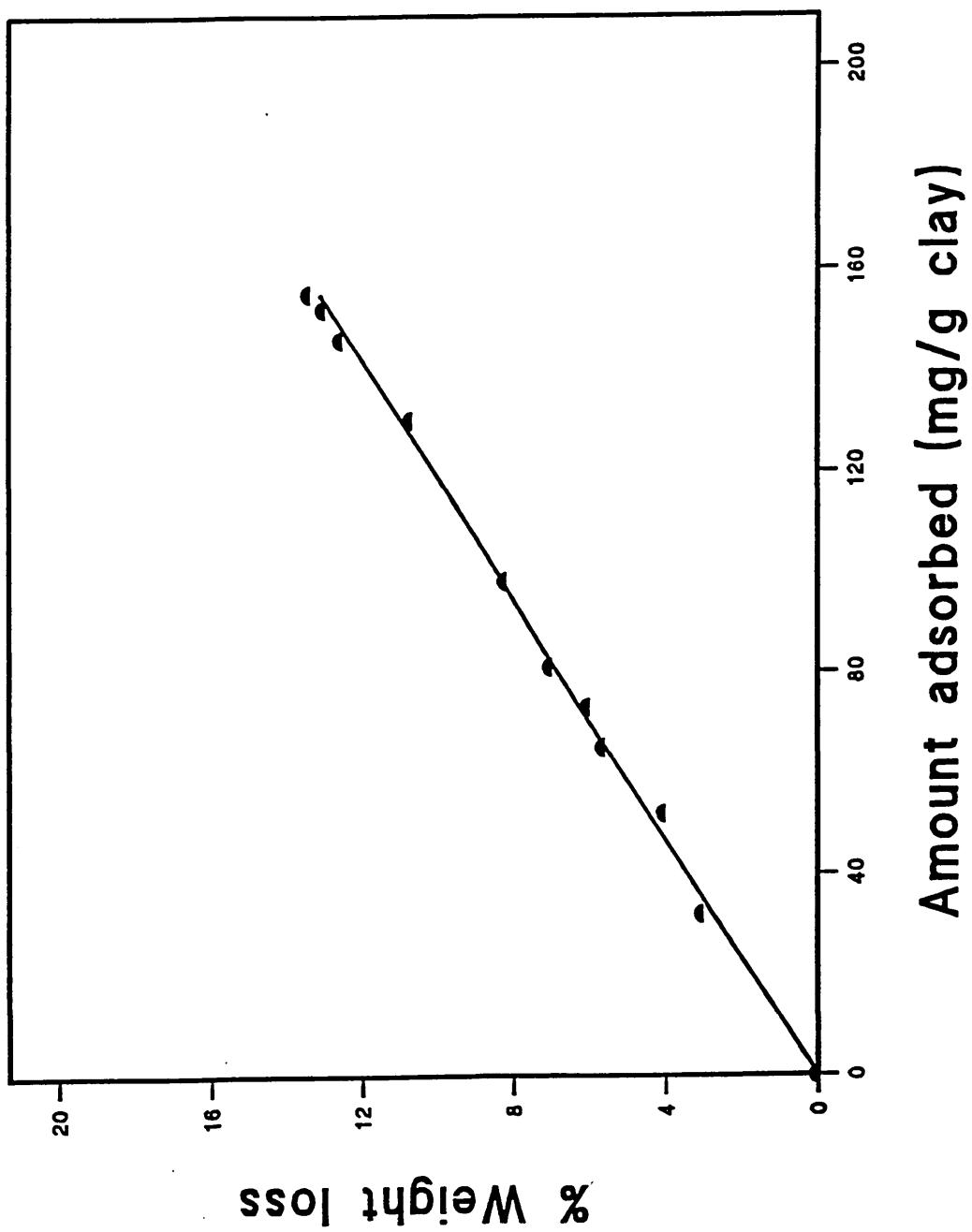


Figure 29. The amount of Magnafloc 206 adsorbed versus the % weight loss.

same breakdown products irrespective of polymer loading. Consequently, TG analysis was occasionally used to confirm polymer loadings.

5.3 SUMMARY OF THE RESULTS OBTAINED FOR (POLY)CATION ADSORPTION.

TMA⁺ cations were adsorbed as expected via ion exchange¹⁴⁷, although van der Waals forces also play a role in the adsorption mechanism. Q_{max} for TMA⁺ adsorption on all clays investigated was lower than that for polymer adsorption due to a lower affinity of the TMA⁺ cations for the clay surface. Q_{max} for TMA⁺ uptake by unsedimented, heterionic SAz-1 was 65 mg/g (72% CEC), as compared to Q_{max} for polymer uptake by unsedimented, heterionic SAz-1 which was 160 mg/g (131% CEC). Theng *et al.*¹⁴⁷ who studied the adsorption of different alkylammonium cations on montmorillonite, stated that as the molecular size of the cations was increased, its affinity for the clay surface increased, which was attributed to the increased contribution of van der Waals forces as the size of the cation was increased.

Polycations are adsorbed via cation exchange of an exchangeable cation associated with the clay for a cationic unit from the polymer. The high affinity of the polycations for the clay surface arises because the net segment-surface interaction energy, ϵ , is equal to approximately 4 kT per cationic unit. As there are many adsorbed segments per polymer molecule there is a large total energy of adsorption. In addition, alternate N groups on the polymer used in this thesis closely match the distance between negative sites on the clay surface¹⁶⁵. In agreement with Breen *et al.*¹⁸⁵, and a French group^{180,186,187,188,189} it is thought that the polymer was adsorbed via a charge neutralisation process which led to flocculation via the electrostatic patch model.

It has been found that the nature of the exchangeable cation associated with the clay and therefore the degree of platelet dispersion, play a major role in determining the quantity of polymer adsorbed. Sedimentation and washing to remove extraneous ions allowed the study of the effect of the exchangeable cation on tactoid formation and hence, on polymer adsorption. Deflocculated suspensions of Na-montmorillonite allow the polymer access to the total surface area of the clay. Conversely, the aggregation of platelets of Cs-montmorillonite results in reduced accessibility of polymer to the clay surface.

It was found that increasing the ionic strength of the medium increased Magnafloc 206 uptake at high initial nitrogen concentrations. Without added salt it is thought that the predominant type of platelet aggregation in heterionic clay suspensions is EF (edge-face). As the saline concentration increases it is thought that increased amounts of EE (edge-edge) bonded platelets are found thus leading to an increase in surface area of the clay and an increase in polymer uptake.

The XRD diffraction data shown here (Figure 27) for the dried samples supports the view that the polymer resides between the layers. Below 50°C, at low polymer loadings, there is polymer present in some layers and water present in others. The data suggests that thermal treatment at 50°C is sufficient to remove much of the water associated with the clay. The basal spacing of polymer exchanged clay is thermally stable to 150°C at low loadings and to over 250°C at higher loadings. TG analysis confirmed the thermal stability of the polymers in the clay. At high polymer loadings, an increase in the quantity of polymer in the interlayer is implied by an increase in the d_{001} spacing to 16.0 Å. This suggests the presence of more than one polymer layer in some interlayers of the clay. Indeed the uptake curves show that polymer is often adsorbed in excess of the CEC.

TMA⁺ cations are present within the interlayer, are more thermally stable than the polymer, and can prop the layers apart even when the system is dehydrated. The TMA-WL complex is thermally stable up to 250°C irrespective of the loading of TMA⁺.

The TG analysis results support the interpretations of the adsorption isotherms. As the polymer loading increases, so does the weight lost during TG analysis. Also, weight loss due to breakdown of the polymer does not begin until after 160°C, with the major loss not occurring until 275°C for higher loadings of polymer, which is consistent with the findings for VT-XRD analysis.

The correlation between the data obtained is not surprising since the samples all underwent similar preparation procedures. A significant point however, is that Kjeldahl, TG and XRD analyses were carried out on dried samples. This may not reflect the true situation in suspension before centrifugation and drying, or when dried samples are resuspended in water. When the samples are dried, some counter ions must remain present to achieve charge neutrality, and it was found that the weight of Cl⁻ increases with increasing amounts of adsorbed polymer. However, the precise mechanism by which these counter ions are incorporated has not yet been determined. Also, samples analysed by Kjeldahl and TG analysis techniques underwent centrifugation procedures which may have affected the natural diffusion of polycationic species by allowing any previously unattached cationic groups to contact exchange sites on the clay particles. This may result in the dried samples exhibiting higher polycation uptake than is found in aqueous suspension during preparation. However, in using these techniques it was not possible to study the situation in suspension and they are not relevant to the work on pollutant adsorption or catalysis where the organoclays are prepared as dry powders.

CHAPTER 6

Investigations into the Adsorption of Pollutants by Organoclays.

6. INTRODUCTION.

As discussed in Chapter 3, the early research into the sorptive behaviour of organoclays was concerned, almost exclusively, with organic vapour uptake by dry modified clay samples. It is generally accepted that the adsorption of organics by clays in aqueous suspension is greatly different from adsorption in nonaqueous systems because water molecules will tend to compete readily for co-ordination sites on strongly solvating exchange cations. Alcohols are capable of competing with water for such sites, and can be adsorbed on Ca-montmorillonite and Na-montmorillonite from aqueous suspension⁸⁰. In addition, long chain molecules capable of permitting van der Waals forces between the molecules and the clay surfaces are preferentially adsorbed from solution. By exchanging organophilic cations onto clays, the adsorption of organic molecules can be increased. Barrer *et al.*⁹ found that smectites exchanged with tetraalkylammonium ions readily adsorbed paraffins and aromatic hydrocarbons from the vapour phase due to the increased amount of available surface area for adsorption.

Later, McBride *et al.*²⁸⁶ began to study adsorption from solution and found that TMA-smectites exhibited a much higher affinity for the adsorption of benzene from water than for the less water-soluble and larger 1,2,4-trichlorobenzene. Moreover, the extent of benzene uptake by the TMA-smectite was much greater than by clays exchanged with either tetraethylammonium (TEA^+) ions, or hexadecyltrimethylammonium (HDTMA^+) ions. The hydrophobic tails from the larger HDTMA^+ ions interact with each other producing an organic phase which acts as a partition medium. Aqueous phase organic contaminants partition into the organic phase created by such organocations. Mechanistically, this is a process of solubilisation analogous to the liquid-liquid partitioning of an organic solute between water and an immiscible organic solvent. The

behaviour of the organic phases of organophilic clays as partition media is shown by the linearity of the sorption isotherms. That TMA⁺ clays function as solid adsorbents is evidenced by non-linear adsorption isotherms, which are frequently of Langmuir form. This aspect was confirmed by Lee *et al.*⁸³. In a partition mechanism, the lower the water solubility, the higher the partition coefficient. Compounds such as benzene that have high water solubilities show strong affinities for TMA-smectite. Despite the fact that TMA-smectite has a much lower organic carbon content (4%), than HDTMA-smectite (17%), the uptake of benzene from aqueous solution was much greater for TMA-smectite.

Barrer and Perry^{105,106} have also argued that the spatial arrangement of TMA⁺ cations in the clay complex would not allow the benzene molecules to lie flat on the siloxane surface but that they would have to adopt a more vertical and less energetically favourable orientation. Boyd and his co-workers Jaynes¹²⁰, Brixie¹²³, Kukkadapu¹¹⁸ and Mortland and Shaobai¹¹⁷, have studied both TMA⁺ and TMPA⁺ (trimethylphenylammonium) exchanged clays and argue that the TMPA⁺ cations on opposing smectite surfaces interact to produce a larger area of free clay surface. They also found that TMPA-clays did not exhibit the marked size selectivity which was observed for TMA-clays.

Lee *et al.*⁸³ have shown shape selectivity for the uptake of aromatic compounds from aqueous solution. Of benzene, toluene, *o*-xylene, *p*-xylene, *o*-dichlorobenzene, 1,2,3-trichlorobenzene and hexachlorocyclohexane (lindane), they found that TMA-smectite shows a clear preference for benzene despite the fact that benzene has the highest water solubility and the lowest molecular weight. They concluded that the

selectivity is related to the shape and size of the benzene molecule and the free space between the TMA⁺ cations on the surface of the water saturated clay. The importance of this is further shown by the fact that the extent of uptake decreased as the size of the solute molecules was increased by adding substituents to the benzene ring. The isotherm for trichlorobenzene is linear indicating the very weak adsorptive interaction of such large molecules with the TMA-smectite in aqueous solution.

Water molecules may associate with the TMA⁺ cations and also solvate mineral sites of the organo-smectite resulting in a reduced interlamellar space which is insufficient to accommodate larger molecules. Lee *et al.*⁸³ concluded that the main factor affecting the degree of adsorption of aromatic molecules by TMA-smectite was the molecular shape/size.

6.1 BENZENE ADSORPTION ON (POLY)CATION EXCHANGED CLAYS.

Figure 30 shows the uptake of benzene on TMA-SWy-1, TMA-SAz-1 and WL with two different loadings of polymer, 25 mg/g (26% CEC) and 146 mg/g (153% CEC) clay respectively. The isotherm for adsorption by TMA-SWy-1 shows a steep initial rise which then becomes more gradual. The isotherm for adsorption by TMA-SAz-1 shows a much shallower rise than TMA-WL, which in turn is much more shallow than TMA-SWy-1, and hence shows that TMA-WL is a better adsorbent than TMA-SAz-1, but poor in comparison to TMA-SWy-1. Hence, it can be seen that the uptake on the low charge smectite, TMA-SWy-1, is much greater than on the high charge, TMA-SAz-1. This effect of layer charge on benzene uptake has also been observed by Lee *et al.*¹¹⁹ and

Jaynes and Boyd¹²⁰. They found that benzene was adsorbed from water by TMA⁺ exchanged clays and that adsorption was more pronounced on clays with a low charge density, which they attributed to the prop-like tetramethylammonium ions being further apart and thus exposing more siloxane surface. Jaynes and Boyd¹²⁰, further investigated this by studying the adsorption of a range of alkylaromatics from water onto TMPA⁺ exchanged clays, in which the charge density on selected clays was reduced using the Hofman-Klemen effect⁵⁵ (Section 2.4.). This approach led to a reduced number of interlayer TMPA⁺ ions and resulted in a change from partition into the organic phase, to adsorption onto the more exposed siloxane surface. The change from partition to adsorption reflects a specific interaction between the adsorbate and the adsorbent and Jaynes and Boyd¹²⁰ again concluded that sorption occurred primarily on the aluminosilicate surfaces.

Q_{\max} for the uptake of benzene on polymer exchanged WL and TMA-SAz-1 (Figure 30), is around 32 - 37 mg/g. There is only a small difference in uptake between the two polymer loadings. The reasons for selecting these particular polymer loadings, which represent low and high loadings respectively, will become clear as the chapter progresses. The results suggest that for benzene, at high equilibrium concentrations, polymer exchanged WL does not make a significantly better adsorbent than TMA-SAz-1. However, the isotherms obtained for the polymer treated WL are a different shape to the TMA-SAz-1 isotherm. At low equilibrium concentrations the isotherms obtained for the polymer treated WL exhibit a higher affinity, as shown by the steeper initial rise, than in the isotherm obtained for TMA-SAz-1. This suggests that at low equilibrium concentrations, polymer treated WL will make a better adsorbent for benzene than TMA-SAz-1.

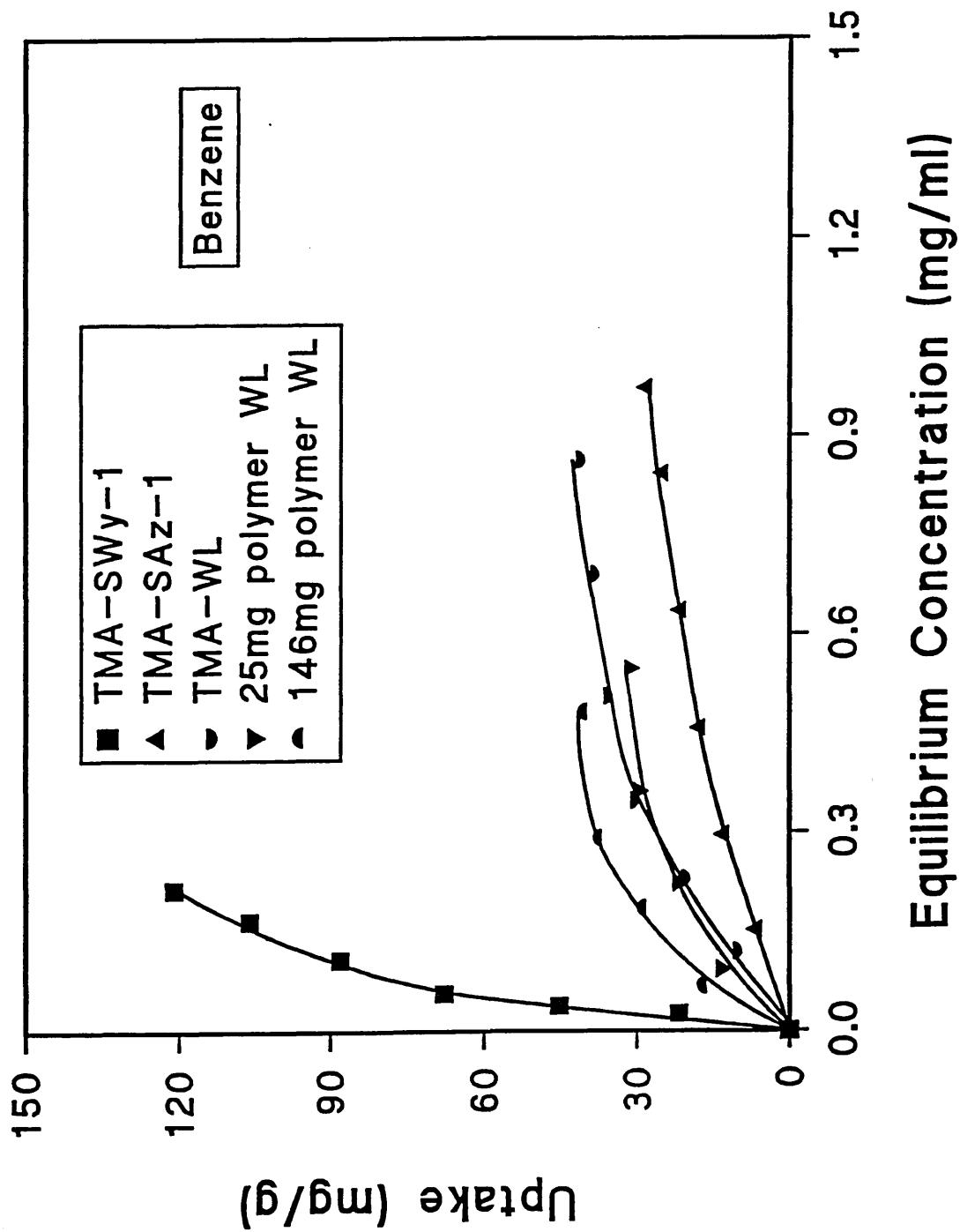


Figure 30. Showing the uptake of benzene on TMA-SWY-1, TMA-SAZ-1 and WL with two different loadings of Magnafloc 206, 25 mg polymer/g clay and 146 mg polymer/g clay.

Based only on the values for the CEC (Table 15), it would be expected that TMA-WL and TMA-SWy-1 should exhibit similar characteristics for the adsorption of benzene. Similar CEC values suggest there should be a similar distribution of TMA^+ , hence, the distance between the cations should be the same, as should the amount of exposed siloxane surface, therefore benzene uptake should be similar. However, it can be seen that TMA-SWy-1 and TMA-WL produce totally different results therefore this theory of exchange cation distribution cannot be the only explanation.

The TMA^+ exchanged sorbents based on SWy-1 and SAz-1 presented herein behaved as reported in the literature for the uptake of benzene and serve as a useful benchmark for the sorption capabilities of the polycation treated clays. McBride *et al.*¹¹⁶ investigated the potential of Cu^{2+} , TMA^+ , TEA^+ (tetraethylammonium) and TPA^+ (tetrapropylammonium) exchanged montmorillonites as sorbents for benzene and phenol. They found that with the exception of Cu-montmorillonite, the surface areas were directly related to the amount of benzene adsorbed, i.e. $\text{TMA}^+ > \text{TEA}^+ > \text{TPA}^+$ with TMA-montmorillonite having a surface area of $210 \text{ m}^2/\text{g}$ (B. E. T.²⁸⁷ determined by N_2 at 78°K), adsorbing 72 mg/g benzene from solution, whilst TPA^+ had a surface area of $37 \text{ m}^2/\text{g}$ and adsorbed no benzene. Cu-montmorillonite, although able to swell in water, also adsorbed minimal amounts of benzene from solution (6 mg/g), which they attributed to the interlamellar space being occupied by the inner and outer hydration sphere of water to Cu^{2+} which the benzene molecules were unable to displace.

McBride *et al.*¹¹⁶ agreed with Barrer and Reay¹⁰⁴ on the arrangement of the organocations within the interlamellar space, i.e. that:

- The small quaternary ammonium cations (TMA^+), were holding the silicate sheets apart but without filling the interlamellar volume.

- The larger ions (TEA^+ and TPA^+), were distorted thus increasing the effective organic radius whilst increasing the distance between the silicate sheets very little. These ions occupy so much interlamellar space that they restrict access of other adsorbates²⁸⁸.

McBride *et al.*¹¹⁶ were able to adsorb 72 mg benzene/g TMA-montmorillonite which they attributed to π interactions with silicate oxygens in agreement with Mortland and Pinnavaia²⁸⁹. Also, since the TMA^+ cation is weakly hydrated, water molecules are easily displaced by benzene as supported by the fact that the interlayers of TMA-montmorillonite are expanded in benzene but are not in water¹¹⁶.

According to the theory of Langmuir adsorption, the maximum adsorption of benzene from solution by TMA-montmorillonite, as observed by McBride *et al.*¹¹⁶, was 132 mg/g which is comparable with the results obtained herein of 122 mg/g by TMA-SWy-1. From surface area measurements they deduced that virtually complete interlamellar adsorption of benzene from water occurred in TMA-montmorillonite. They surmised that the benzene molecules were unlikely to be orientated between the sheets with the plane of the aromatic ring perpendicular to the silicate sheet since this orientation would prevent π interactions with the surface. As was observed by Pinnavaia and Mortland²⁹⁰ for toluene on Cu-montmorillonite, the orientation of the benzene molecules is assumed to be tilted as the basal spacing of TMA-montmorillonite in benzene is 15.0 Å.

Figure 31 shows the uptake of benzene on polymer exchanged WL and polymer exchanged Cs-WL. As discussed in the previous chapter (Section 5.2.1), Cs-WL has a different floc structure to heterionic WL. It can be seen that by exchanging the natural cations of the clay with Cs^+ ions the uptake of benzene is reduced to virtually zero. Treating the Cs-exchanged clay with large amounts of polymer improves the uptake of benzene but still does not exceed that found for polymer exchanged heterionic WL. The gradient of the curves increases with polymer loading and hence organic carbon content which suggests a partition mechanism. Indeed large loadings of polymer are thought to restrict access to the siloxane surface. TMA-SWy-1 (Figure 30), however, exhibits significantly enhanced uptake compared to any of the clays studied here. $Q_{\max} = 122$ mg/g for the concentrations studied making TMA-SWy-1 the best adsorbent for benzene of the clays investigated.

As discussed in the introduction to this chapter, Lee *et al.*⁸³ found that despite TMA-smectite having a much lower organic carbon content (4%), than HDTMA⁺ (hexadecylammonium) exchanged smectite (17%), the uptake of benzene from aqueous solution was much greater for TMA-smectite. Furthermore, the amount sorbed increased as the amount of available siloxane surface increased, thus supporting the view that the siloxane surface was hydrophobic. The aromatics were considered to be adsorbed onto the exposed siloxane surface.

Also, as discussed above, McBride *et al.*²⁸⁶ also found that uptake of benzene decreased with increasing organic carbon content and this agrees in general with the results presented herein. The high organic carbon content of HDTMA-smectite is analogous to the situation on the polymer exchanged clays which also adsorbed comparably little

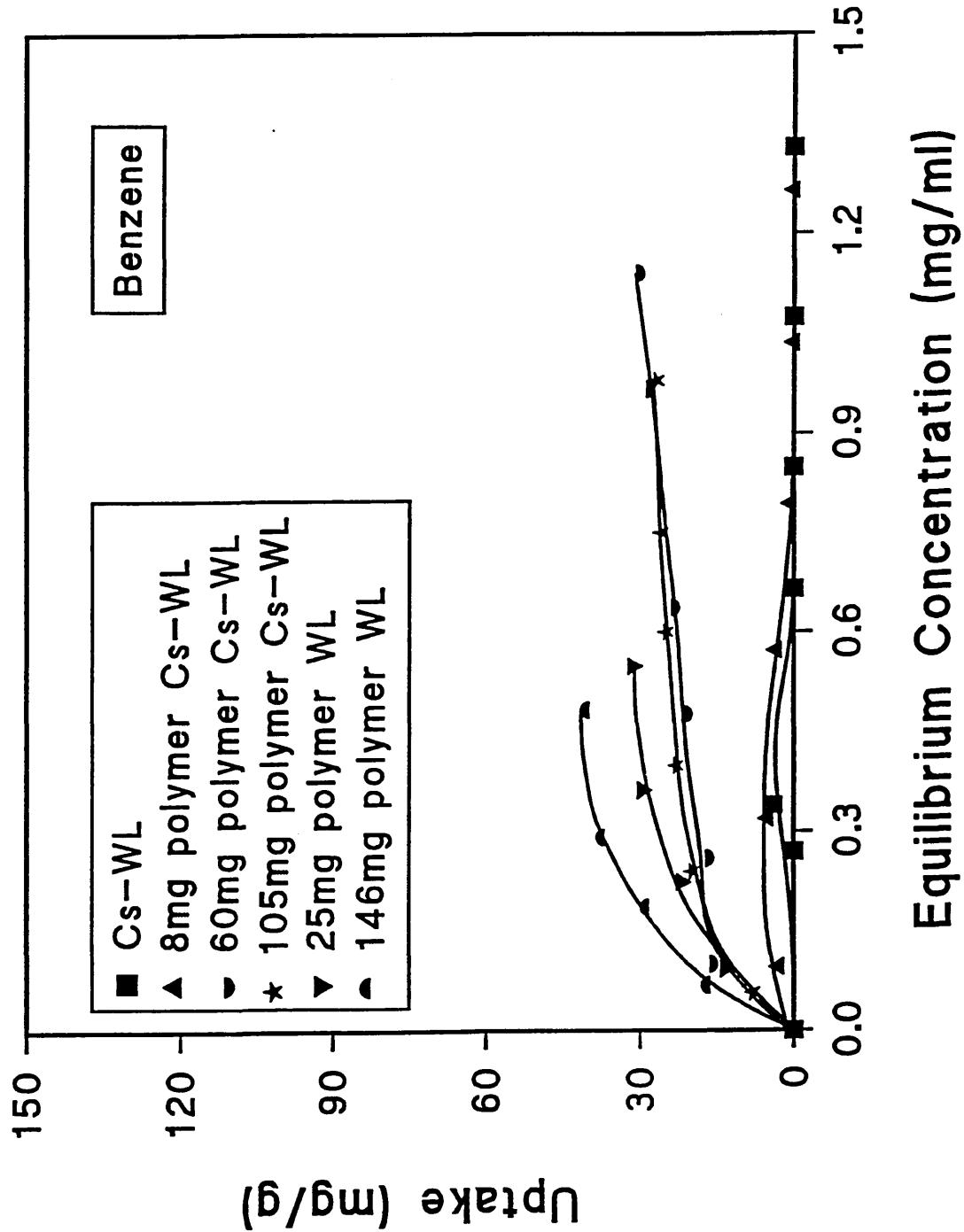


Figure 31. Showing the uptake of benzene on Magnafloc 206 exchanged WL and Magnafloc 206 exchanged Cs-WL. (Loadings are mg polymer/g clay)

benzene from solution as compared to TMA-SWy-1 as a result of decreased accessibility to the siloxane surface.

6.2 ADSORPTION OF *p*-NITROPHENOL ON (POLY)CATION EXCHANGED CLAYS.

Figure 32 shows the uptake of *p*-nitrophenol on SWy-1 exchanged with different loadings of polymer. On SWy-1 alone the uptake gave an S type⁹⁷ isotherm. This suggests that at very low *p*-nitrophenol concentrations only small amounts are adsorbed, but as adsorption increases and patches of *p*-nitrophenol form on the clay surface, the surface becomes more hydrophobic. This encourages the adsorption of more *p*-nitrophenol as seen by the increase in gradient of the uptake curve. Finally, at higher *p*-nitrophenol concentrations, the amount adsorbed does not increase significantly as shown by the decrease in gradient. This change in hydrophobicity, with a small amount of adsorption encouraging further adsorption, has been seen by Billingham *et al.*²⁹¹. They titrated pyridine onto Al-SWy-1 in the presence of benzene and studied, in-situ, the change in absorbance of various infrared bands. They found that initially, only a small quantity of benzene was adsorbed, but as pyridine displaced water from the clay complex pyridinium was formed which created an organoclay complex. As the pyridine loading increased, and hence the hydrophobicity of the clay surface increased, the adsorption of benzene increased.

Exchanging the clay surface with small amounts of polymer (28 mg/g and 46 mg/g, Figure 32), increases the adsorption of *p*-nitrophenol by expanding the clay layers and allowing greater access to the clay surface. The shape of the uptake curves at these

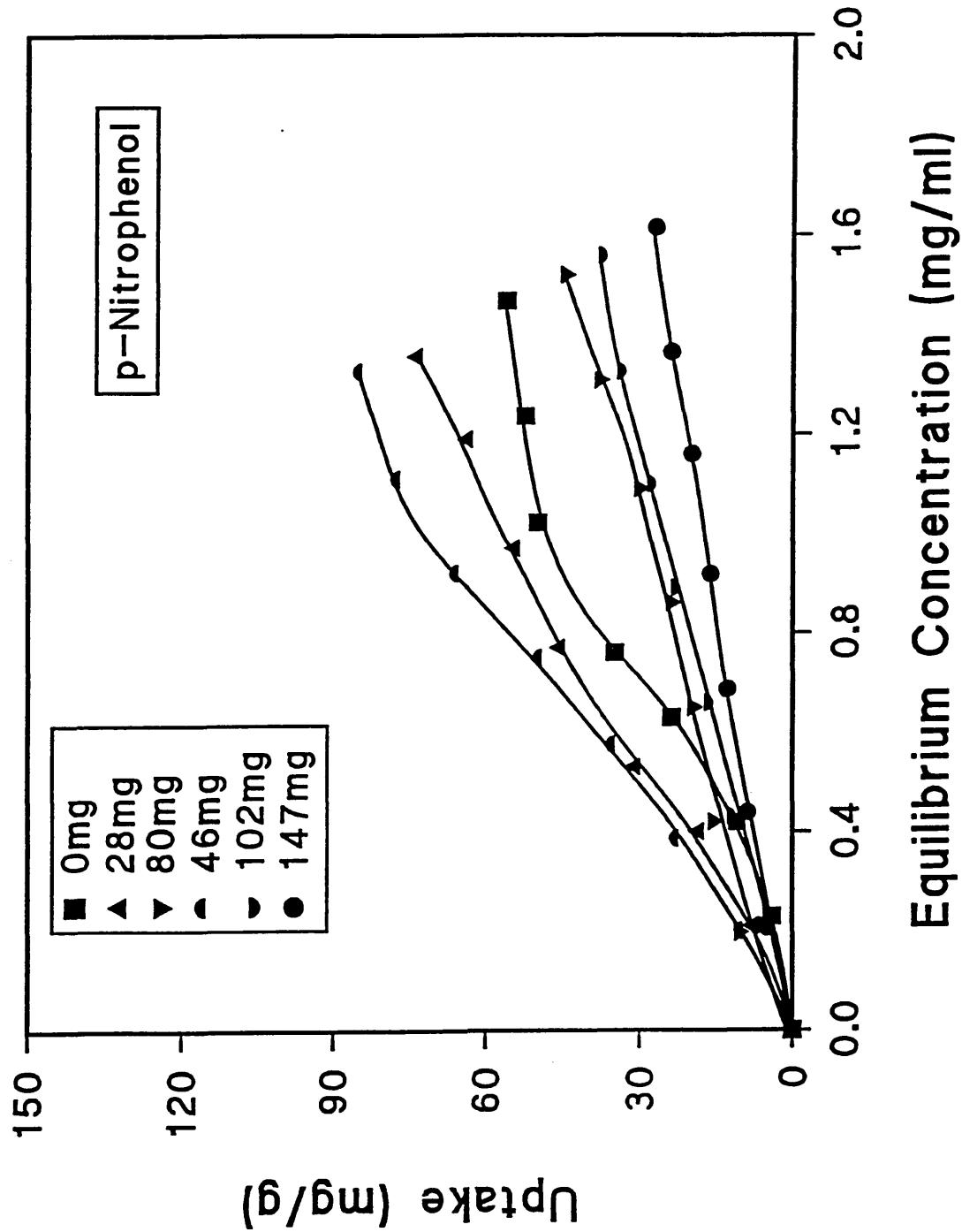


Figure 32. Showing the uptake of *p*-nitrophenol on SWy-1 with different loadings of Magnafloc 206.
(Loadings are mg polymer/g clay).

loadings is typical of an adsorption mechanism. It can be seen that the optimum loading of polymer/g clay is 46 mg/g which gives $Q_{\max} = 85$ mg *p*-nitrophenol/g clay. As the polymer loading increases above 46 mg/g the amount of *p*-nitrophenol adsorbed decreases and at loadings of > 80 mg/g is lower than for SWy-1 only. This is thought to be due to reduced access of the *p*-nitrophenol to the clay surface. Loadings of 80, 102 and 147 mg polymer/g clay show straight line curves which are typical of partition into the organic phase. However, the gradient of these curves decreases with increasing organic carbon content (polymer loading), which conflicts with a partition mechanism. It is thought that as polymer loading increases, the clay layers become more packed with polymer chains which reduces the swelling ability of the clay by holding the layers together. Increasing numbers of polymer chains will increase the combined strength of the bond between the clay layers. This is supported by Billingham *et al.*²⁸⁵ who have shown that at high loadings of polycation, bentonite does not swell in polyethylene glycol (PEG), which indicates that the clays layers are bound together. Hence, at high polymer loadings there will be large areas of organic carbon (polycation) which are not accessible to interact with *p*-nitrophenol. Therefore, the adsorption mechanism is one of partition but only into the organic carbon (polycation) which is easily accessible at the outer regions and not 'hidden' behind numerous other polymer chains. A schematic representation of this is shown in Figure 33.

Boyd²⁹² studied the adsorption of substituted phenols by soils and found that the introduction of -CH₃, -OCH₃, -NO₂, or -Cl groups to phenol resulted in increased adsorption due to decreased water solubility. Also, with the exception of *o*-nitrophenol, adsorption by soils (organic matter and clay), was generally greater than predicted by hydrophobic sorption, which he attributed to hydrogen bond formation.

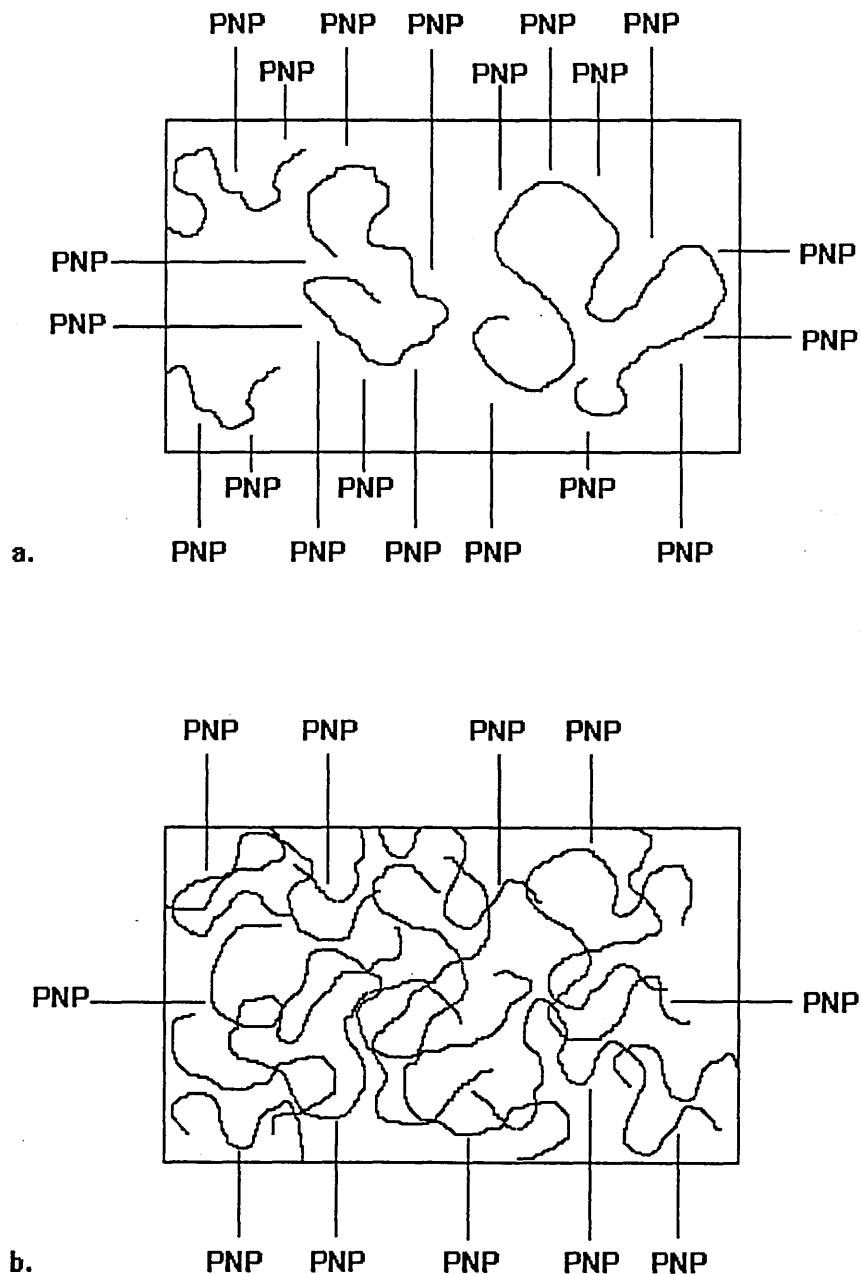


Figure 33. Showing that at low polymer loadings (a) *p*-nitrophenol has easy access to a large amount of silicate surface, whilst at high polymer loadings (b) there are large areas of polycation which is inaccessible to *p*-nitrophenol.

The uptake of *p*-nitrophenol by 2 loadings of PAA (poly(allylamine hydrochloride) on SWy-1 is shown in Figure 34 with uptake on SWy-1 only and Magnafloc 206 exchanged SWy-1 shown for comparison. It can be seen that SWy-1 exchanged with 15 or 30 mg/g PAA adsorbs less *p*-nitrophenol than SWy-1 only, which was also noted for higher loadings (≥ 80 mg/g) of Magnafloc 206. Also, as the PAA loading increases the uptake of *p*-nitrophenol decreases. As both loadings appear to give a linear curve typical of a partition mechanism, *p*-nitrophenol uptake is again thought to be related to the amount of available carbon. However, similar loadings of Magnafloc 206 (28 mg/g) and PAA (30 mg/g) result in quite different amounts of *p*-nitrophenol uptake, i.e. $Q_{\max} = 74$ mg/g (Magnafloc 206) and $Q_{\max} = 32$ mg/g (PAA). This may be related to the structure of the monomer units of the polymers (Figure 18a, 18b) and hence the floc structure in solution, although the exact mechanism is not clear. Despite PAA being completely hydrophobic, PAA exchanged SWy-1 does not produce as good an adsorbent as Magnafloc 206 exchanged SWy-1 for the loadings studied.

The effect of the nature of the clay on *p*-nitrophenol adsorption is shown in Figure 35. It can be seen that TMA-SWy-1 is the best adsorbent of *p*-nitrophenol of all the systems studied ($Q_{\max} = 110$ mg *p*-nitrophenol/g clay). Conversely, TMA-WL, TMA-WL3 and TMA-SA_z-1, show negligible uptake of *p*-nitrophenol ($Q_{\max} < 20$ mg/g). The behaviour of TMA-SA_z-1 is expected since, as discussed above, there is reduced mineral surface area in TMA-SA_z-1 due to the close packing of the TMA cations. These findings are in contrast to the findings for benzene adsorption where TMA-WL adsorbed more benzene than TMA-SA_z-1. As was anticipated for benzene uptake based on CEC values, TMA-WL was anticipated to have a sorption capacity similar to that of TMA-SWy-1 but this was not the case.

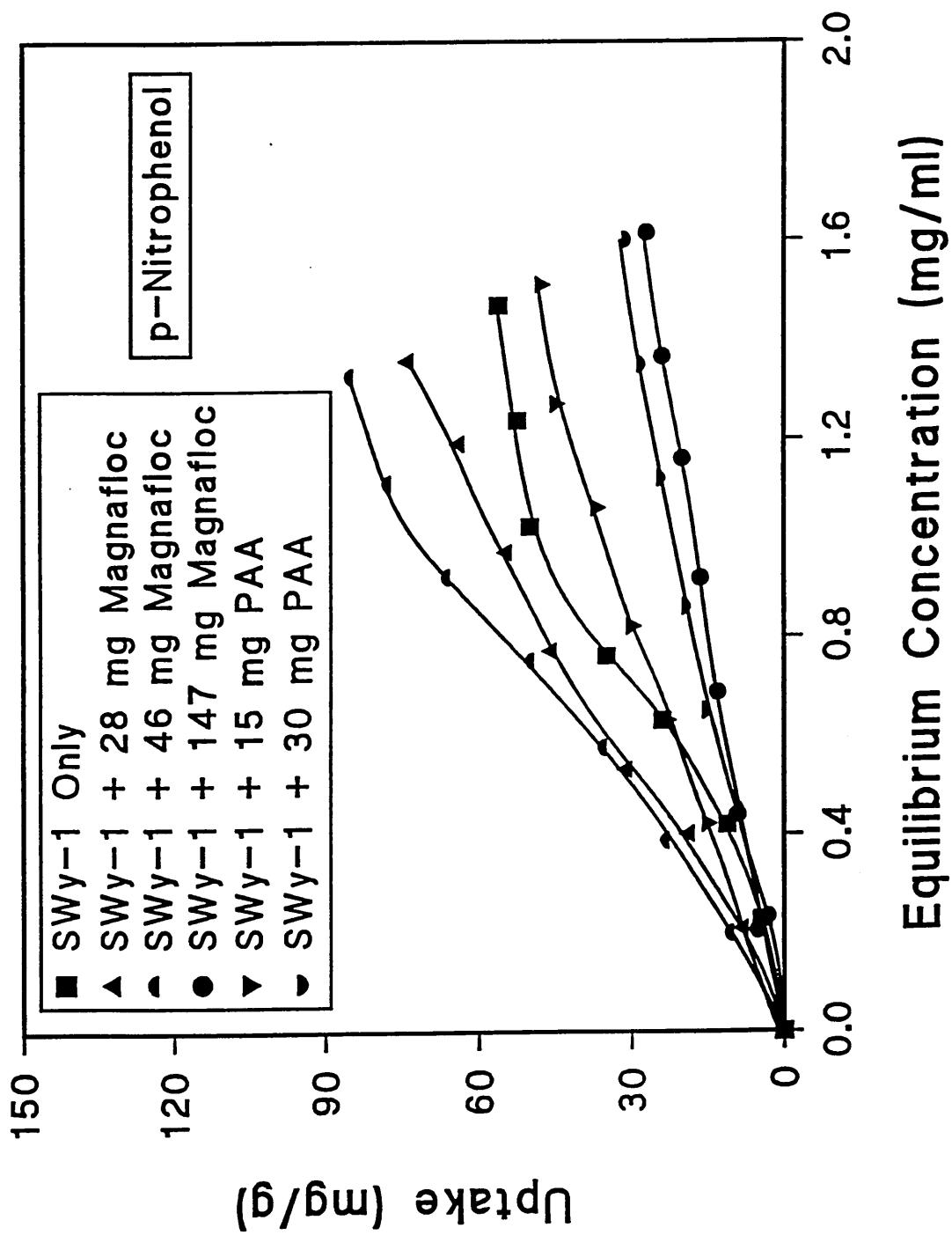


Figure 34. Showing the uptake of *p*-nitrophenol by SWy-1 only, SWy-1 with 2 loadings of PAA and SWy-1 with three loadings of Magnafloc 206. (Loadings are mg polymer/g clay).

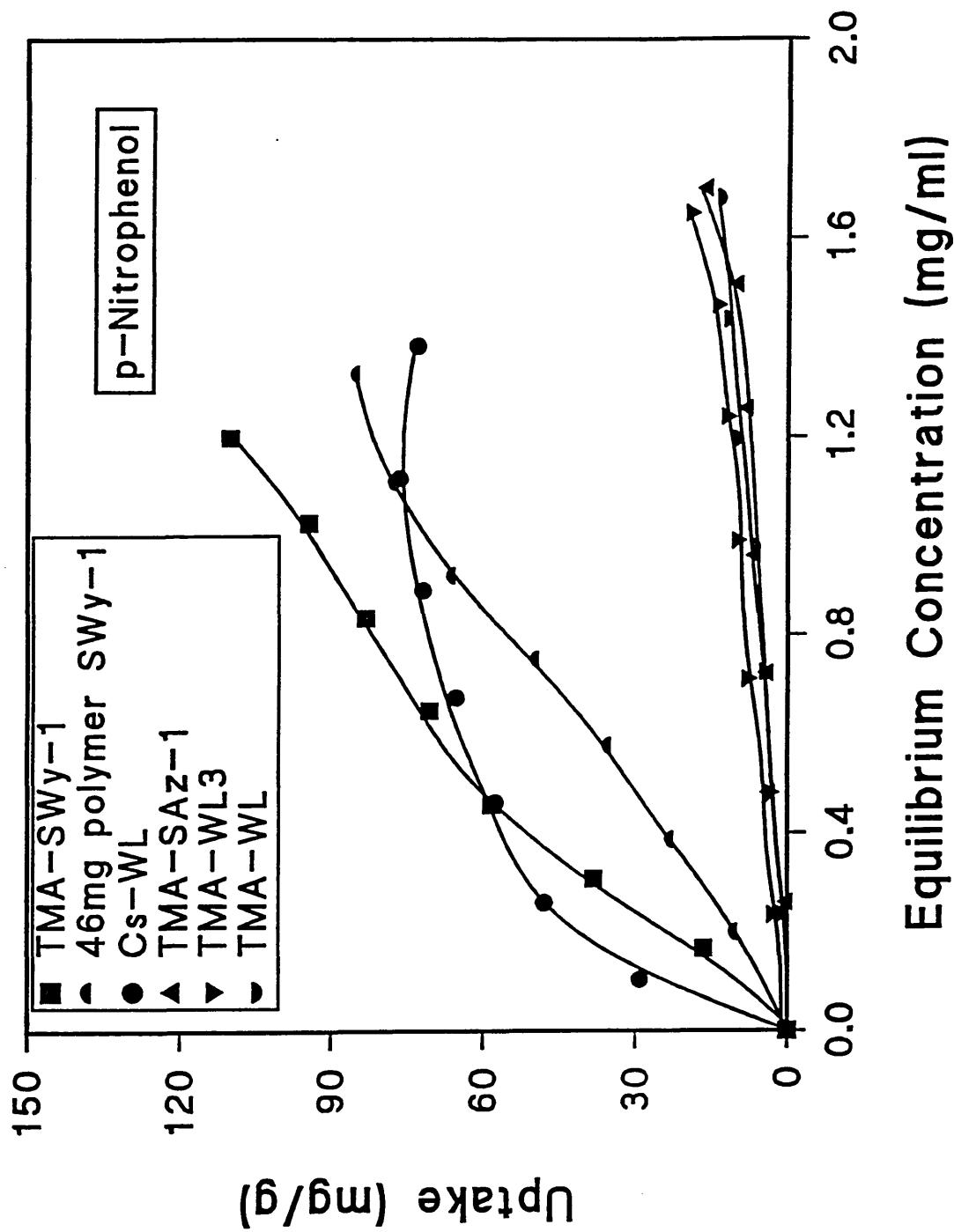


Figure 35. Showing how the nature of the clay affects *p*-nitrophenol adsorption.

The uptake by Cs-WL is significant and comparable to SWy-1 exchanged with the optimum loading of polymer (Figure 35). However, *p*-nitrophenol shows a much higher affinity for Cs-WL than for polymer exchanged SWy-1 as shown by the initial steep rise in the uptake isotherm. These results suggest that there is a direct interaction between *p*-nitrophenol and the Cs⁺ cations since the CEC of Cs-WL is 0.81 meq/g and Q_{max} = 0.5 mmol *p*-nitrophenol/g, therefore there is one *p*-nitrophenol molecule associated with 62% of the available Cs⁺ cations. This is investigated further in Figure 36.

Figure 36 shows how different polymer loadings on Cs-WL influenced *p*-nitrophenol uptake. TMA-WL and TMA-SWy-1 are shown for comparison. Again, in contrast to the findings for benzene adsorption, it was found that increasing the loading of polymer decreased the uptake of *p*-nitrophenol. At a loading of 105 mg polymer/g Cs-WL (121% CEC), the uptake is minimal but this would be anticipated if *p*-nitrophenol adsorption is via interaction with Cs⁺ ions. Breen *et al.*¹⁸⁵ have shown by ¹³³Cs NMR that Cs⁺ ions are effectively displaced by a polymer of the same monomer structure as Magnafloc 206, ($[Me_2NCH_2CHOHCH_2]_n^+$) but of higher molecular weight (100,000). Figure 24 shows that at an intermediate loading of 60 mg/g polymer (Q_{max} = 120 mg/g) on Cs-WL, only half of the Cs⁺ ions are displaced by polymer. Noticeably, displacement of half the Cs⁺ ions coincides with a reduction in *p*-nitrophenol uptake of about half, 73 mg/g c.f. 35 mg/g, thus supporting the theory that *p*-nitrophenol interacts with available Cs⁺ ions rather than the clay surface. This sort of phenomenon has been seen before by Haderlein and Schwarzenbach²⁹³ who studied the absorbance of catechol (1,2-dihydroxybenzene) and *o*-nitrophenol by kaolinite exchanged with K⁺, Rb⁺, Cs⁺, Na⁺, Mg²⁺, Ca²⁺ and Al³⁺ ions. They found that uptake of catechol was independent of the exchange ion and concluded that catechol, a bidentate oxygen donor, formed

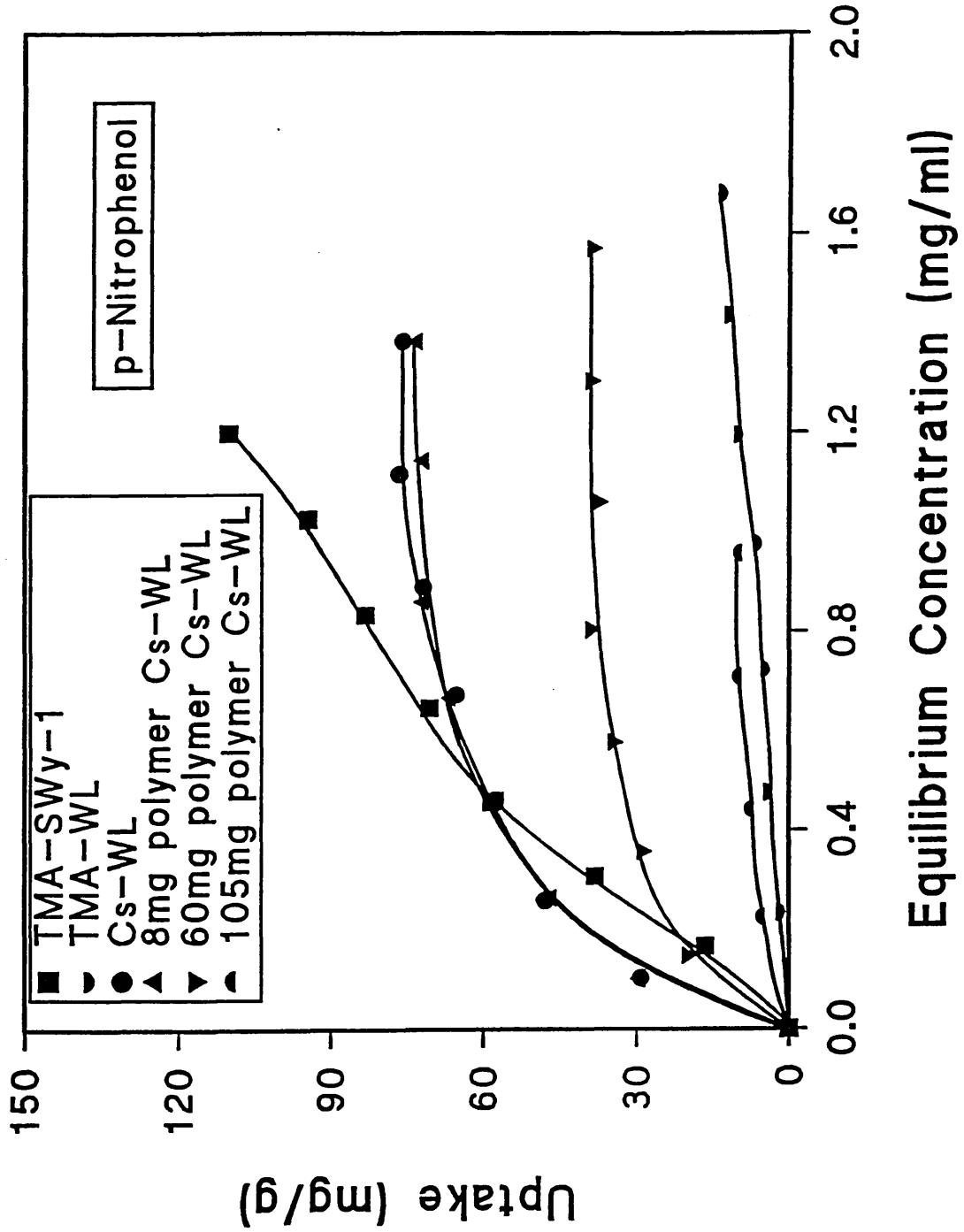


Figure 36. Showing how different polymer loadings on Cs-WL influences *p*-nitrophenol uptake. TMA-WL and TMA-SW_y-1 are shown for comparison. (Loadings are mg polymer/g clay).

complexes with the surface Al-OH groups by ligand exchange mechanisms. Conversely, they found that kaolinite exchanged with the strongly hydrated cations (Na^+ , Mg^{2+} , Ca^{2+} and Al^{3+} ions), showed minimal adsorption of *o*-nitrophenol, whereas kaolinite exchanged with the weakly hydrated cations adsorbed *o*-nitrophenol increasing as K-kaolinite < Rb-kaolinite < Cs-kaolinite. They concluded that the nature of the exchange cation associated with kaolinite was critical in determining the adsorption of *o*-nitrophenol since adsorption was associated with the cations rather than the siloxane surface.

6.3 SUMMARY OF RESULTS FOR POLLUTANT ADSORPTION.

Two potential adsorption sites exist in organoclays. When exchanged with small quaternary ammonium ions, e.g. TMA^+ , organic contaminants could interact with the aluminosilicate mineral surface and/or with the TMA^+ exchange ions. The uptake of both benzene and *p*-nitrophenol by TMA^+ treated high charge SAz-1, has been found to be reduced compared to TMA^+ treated low charge SWy-1 (Figures 30 and 32). In SAz-1 there will be closer packing of adsorbed TMA^+ cations resulting in less siloxane surface area being available. This suggests that the predominant adsorption site is the siloxane surface in the clay interlayers, as proposed by Jaynes and Boyd¹²⁰, although there are also steric constraints. As the cation packing density increases, access to the clay surface becomes more difficult. This problem is exaggerated by the hydration of TMA^+ in water which further reduces accessibility.

There is a slightly greater uptake of benzene on TMA-SWy-1 than *p*-nitrophenol on TMA-SWy-1 . $Q_{\max} = 122 \text{ mg/g}$ for benzene and $Q_{\max} = 108 \text{ mg/g}$ for *p*-nitrophenol. This is in agreement with the findings for shape selectivity of Lee *et al.*³⁸ who found that

uptake decreased as the size of the solute molecules was increased by adding substituents to the benzene ring, as discussed in the introduction to this chapter.

TMA-SWy-1 and TMA-WL were anticipated to exhibit the same behaviour for the adsorption of benzene and *p*-nitrophenol based on their similar CEC values, which suggest a similar distribution of TMA⁺ cations. However, they showed totally different abilities, with TMA-WL actually behaving more like TMA-SAz-1 which has a much higher CEC. Hence, this cannot be the only explanation although the full mechanism is not yet fully understood.

The polymers used in this work are very small in size when compared to the size of the clay particles. When the polymer is adsorbed onto the surface of the clay there may not be a uniform neutralisation of charge. This uneven distribution of charge leads to an extra attractive contribution to the interaction energy between two such particles. Flocculation occurs as a result of a positively charged, polymer rich patch of one particle coming into contact with a negatively charged, polymer free patch on another (electrostatic patch model, Section 3.11.1). This results in face to face aggregation which will reduce the available surface area. This is different to TMA⁺ treated clays which tend to form deflocculated aggregates. Therefore, an increase in polymer loading may lead to increased aggregation which will further reduce the available surface area.

The VT-XRD results presented herein show that at low loadings of polymer where the CEC is not satisfied, the polymer is segregated in different interlayers and has the ability to swell further on the addition of adsorbing species (e.g. benzene), thus allowing an adsorption mechanism. This is in agreement with Billingham *et al.*²⁸⁵ who found that at

low loadings of polymer, SWy-1 could adsorb PEG (polyethylene glycol). However, at high polymer loadings the strong attractive forces between the polymer and the clay sheets prevented the adsorbed PEG from separating the sheets and further swelling the clay. Hence, high polymer loadings will prevent adsorption onto the silicate surface and allow partition into only a small amount of organic carbon (polycation) which is easily accessible at the edges of the sheets. Large areas of organic carbon will be 'hidden' by the numerous polymer chains and hence be inaccessible.

It has been shown that only low loadings of Magnafloc 206 (46 mg/g or less), are better at adsorbing *p*-nitrophenol than the untreated clay which supports the theory that the siloxane surface is the predominant adsorption site. Higher loadings of polymer (> 46 mg/g), hinder the adsorption of the organic species by preventing access to the siloxane surface which may be a steric effect, although the floc structure and particle size distribution of the treated clays may also be contributing. This idea is supported by the observation that the fully hydrophobic polymer (PAA) showed a reduced ability to adsorb *p*-nitrophenol compared to the polymer containing an -OH group (Magnafloc 206). The different nature of the monomer units is likely to affect the floc structure.

In addition, all of the modified clays used here have been dried, then rehydrated in order to study adsorption from solution. How the clay preparation and drying stages affect the structure of the (poly)cation exchanged clays is not fully understood, but this may be significant.

It has also been shown that uptake of *p*-nitrophenol to polymer exchanged Cs-SWy-1 is dependant on accessibility to the Cs⁺ cations.

CHAPTER 7

Investigations into the Catalytic Activity of Organoclays.

7. INTRODUCTION.

Commercial acid treated clays are normally prepared using a fixed quantity of acid chosen to remove the desired proportion of cations from the octahedral sheet²²⁸ yet few investigations have addressed how the catalytic activity varies with octahedral sheet depletion²⁷⁰.

During acid-activation of clays the octahedral ions are leached out, the nitrogen surface area increases, the number (and type) of acid sites changes as do the sorptive and catalytic properties. These properties generally maximise under intermediate activation conditions and subsequently decrease as the product takes on the properties of amorphous silica, which has been identified as the final product of acid leaching^{218,219,237}. It is now widely accepted that clays with a high octahedral Mg²⁺ content leach more readily than those which have a high octahedral Al³⁺ population^{206,215,216,218,219} and recent reports have established that clays with a high octahedral Fe^{2+/3+} content also leach rapidly^{223,294}. An extensive investigation into the acid-leaching of a range of smectites (selected for their differing octahedral ion content), has shown that the elemental composition of the starting material did not make a significant contribution to the catalytic activity for the chosen test reaction but did play a key role in determining the severity of the activation conditions required for the optimisation of the catalytic activity²⁹⁴. The extent of acid dissolution can significantly influence the activity of the catalyst for a particular reaction whether it is employed as a support²¹¹ or as a catalyst in its own right^{270,294}.

As discussed previously in this thesis (Sections 3.4.1 and 3.4.2), it has long been established that the hydrophilic aluminosilicate surface of swelling clays can be rendered

hydrophobic by exchanging the naturally occurring inorganic cations with organocations. This knowledge coupled with the recent enhancement of the catalytic activity of pillared clays, via pillarizing acid-activated clays^{20,262}, led to consideration of acid treated organoclays as catalysts for reactions in non-polar media.

The conversion of α -pinene to camphene, the chosen test reaction, has industrial significance because camphene is an intermediate in the synthesis of camphor, which has value due to its aroma and pharmaceutical properties²⁶. Acidified titanium oxide is usually employed in the transformation of α -pinene to camphene²⁷⁷, although recent studies have considered the use of zeolites^{278,295}, pillared interlayer clays (PILCs)²⁷⁸ and (both crystalline and amorphous) zirconium and tin phosphates²⁸⁰. Acid-activated polycation-exchanged smectites are used here for the conversion of α -pinene to camphene, via ring expansion, and limonene, via ring opening²⁷⁵. The aim is to produce cost-effective, hydrophobic catalysts of relatively high acidity in a short time using simple exchange procedures. This approach explores the resistance of organoclays to octahedral ion leaching and has the potential to reduce the concentration of Al^{3+} , Mg^{2+} and Fe^{2+3+} in effluent flows from the leaching process. Cognisant of the importance of the octahedral sheet composition on acid leaching, several starting clays of different octahedral composition have been used, which have been the focus of acid leaching studies previously^{218,219,294,298}, to evaluate the properties of the resulting catalysts. The results are compared with the yields from novel acid-activated organoclays prepared herein.

7.1 SAMPLES.

Tables 7 - 11 which show sample designations and the conditions used are presented again here for reference.

Analysis of the organoclays provided by co-workers in Bratislava is given in this chapter as these clays are investigated solely as catalysts. When discussed in general terms, the organoclays provided by co-workers will be referred to as Slovak clays. Clays that are not exchanged with organic cations, or acid-activated are termed 'base clays'.

Since some collaborative work was involved, all data is not available for all samples. For example, % carbon values and the amount of Ca^{2+} displaced is available only for Slovak samples since the samples were analysed in Bratislava. XRF analysis of the Slovak samples was not possible as there was insufficient sample available.

7.2 ANALYSIS.

7.2.1 XRD Analysis.

The d-spacings for the organoclays are given in Table 17. Spacings of approximately 14 Å, as exhibited by the TMA^+ exchanged samples, indicate that the organocations are lying flat on the basal surface of the clay. The other samples show an increase in d-spacing as the loading of organocation increases, which supports the findings of others^{155,156,157,158} as discussed in Section 3.9.3. The spacing of 17.8 Å suggests a bilayer has been formed, whereas spacings in excess of 20 Å can be attributed to either a pseudotrimolecular arrangement of organocations or a structure in which the

Code	Organic cation (OC)	mmol OC offered	Volume HCl (ml)	HCl Concn.	Treatment Temp.	Acid contact time (minutes)
JP-0	None	-----	None	-----	-----	-----
JP-2	None	-----	2	0.1 M	25°C	60
JP-4	None	-----	4	0.1 M	25°C	60
JP-M1	TMA	0.25	None	-----	-----	-----
JP-M2	TMA	0.50	None	-----	-----	-----
JP-M3	TMA	1.00	None	-----	-----	-----
JP-M1-2	TMA	0.25	2	0.1 M	25°C	60
JP-M1-4	TMA	0.25	4	0.1 M	25°C	60
JP-M2-2	TMA	0.50	2	0.1 M	25°C	60
JP-M2-4	TMA	0.50	4	0.1 M	25°C	60
JP-M3-2	TMA	1.00	2	0.1 M	25°C	60
JP-M3-4	TMA	1.00	4	0.1 M	25°C	60
JP-L1	DDTMA	0.25	None	-----	-----	-----
JP-L2	DDTMA	0.50	None	-----	-----	-----
JP-L3	DDTMA	1.00	None	-----	-----	-----
JP-L1-2	DDTMA	0.25	2	0.1 M	25°C	60
JP-L1-4	DDTMA	0.25	4	0.1 M	25°C	60
JP-L2-2	DDTMA	0.50	2	0.1 M	25°C	60
JP-L2-4	DDTMA	0.50	4	0.1 M	25°C	60
JP-L3-2	DDTMA	1.00	2	0.1 M	25°C	60
JP-L3-4	DDTMA	1.00	4	0.1 M	25°C	60
JP-O1	ODTMA	0.25	None	-----	-----	-----
JP-O2	ODTMA	0.50	None	-----	-----	-----
JP-O3	ODTMA	1.00	None	-----	-----	-----
JP-O1-2	ODTMA	0.25	2	0.1 M	25°C	60
JP-O1-4	ODTMA	0.25	4	0.1 M	25°C	60
JP-O2-2	ODTMA	0.50	2	0.1 M	25°C	60
JP-O2-4	ODTMA	0.50	4	0.1 M	25°C	60
JP-O3-2	ODTMA	1.00	2	0.1 M	25°C	60
JP-O3-4	ODTMA	1.00	4	0.1 M	25°C	60

TMA = Tetramethylammonium

DDTMA = Dodecyltrimethylammonium

ODTMA = Octadecyltrimethylammonium

Table 7. Showing the extents of organic cation exchange and acid treatments for Jelsovy Potok (JP) derived samples.

Code	Organic cation (OC)	mmol OC offered	Volume HCl (ml)	HCl Concn.	Treatment Temp.	Acid contact time (minutes)
ST-0	None	-----	None	-----	-----	-----
ST-2	None	-----	2	0.1 M	25°C	60
ST-4	None	-----	4	0.1 M	25°C	60
ST-60	None	-----	60	1.0 M	25°C	60
ST-M1	TMA	0.25	None	-----	-----	-----
ST-M2	TMA	0.50	None	-----	-----	-----
ST-M3	TMA	1.00	None	-----	-----	-----
ST-M1-2	TMA	0.25	2	0.1 M	25°C	60
ST-M1-60	TMA	0.25	60	1.0 M	25°C	60
ST-M2-2	TMA	0.50	2	0.1 M	25°C	60
ST-M2-60	TMA	0.50	60	1.0 M	25°C	60
ST-M3-2	TMA	1.00	2	0.1 M	25°C	60
ST-M3-60	TMA	1.00	60	1.0 M	25°C	60
ST-L1	DDTMA	0.25	None	-----	-----	-----
ST-L2	DDTMA	0.50	None	-----	-----	-----
ST-L3	DDTMA	1.00	None	-----	-----	-----
ST-L1-2	DDTMA	0.25	2	0.1 M	25°C	60
ST-L1-60	DDTMA	0.25	60	1.0 M	25°C	60
ST-L2-2	DDTMA	0.50	2	0.1 M	25°C	60
ST-L2-60	DDTMA	0.50	60	1.0 M	25°C	60
ST-L3-2	DDTMA	1.00	2	0.1 M	25°C	60
ST-L3-60	DDTMA	1.00	60	1.0 M	25°C	60
ST-O1	ODTMA	0.25	None	-----	-----	-----
ST-O2	ODTMA	0.50	None	-----	-----	-----
ST-O3	ODTMA	1.00	None	-----	-----	-----
ST-O1-2	ODTMA	0.25	2	0.1 M	25°C	60
ST-O1-60	ODTMA	0.25	60	1.0 M	25°C	60
ST-O2-2	ODTMA	0.50	2	0.1 M	25°C	60
ST-O2-60	ODTMA	0.50	60	1.0 M	25°C	60
ST-O3-2	ODTMA	1.00	2	0.1 M	25°C	60
ST-O3-60	ODTMA	1.00	60	1.0 M	25°C	60

TMA = Tetramethylammonium

DDTMA = Dodecyltrimethylammonium

ODTMA = Octadecyltrimethylammonium

Table 8. Showing the extents of organic cation exchange and acid treatments for Stebno (ST) derived samples.

Code	Organic cation (OC)	mmol OC offered	Volume HCl (ml)	HCl Concn.	Treatment Temp.	Acid contact time (minutes)
SWa-0	None	-----	None	-----	-----	-----
SWa-2	None	-----	2	0.1 M	25°C	60
SWa-4	None	-----	4	0.1 M	25°C	60
SWa-60	None	-----	60	1.0 M	90°C	60
SWa-M1	TMA	0.25	None	-----	-----	-----
SWa-M2	TMA	0.50	None	-----	-----	-----
SWa-M3	TMA	1.00	None	-----	-----	-----
SWa-M1-2	TMA	0.25	2	0.1 M	25°C	60
SWa-M1-60	TMA	0.25	60	1.0 M	90°C	60
SWa-M2-2	TMA	0.50	2	0.1 M	25°C	60
SWa-M2-60	TMA	0.50	60	1.0 M	90°C	60
SWa-M3-2	TMA	1.00	2	0.1 M	25°C	60
SWa-M3-60	TMA	1.00	60	1.0 M	90°C	60
SWa-L1	DDTMA	0.25	None	-----	-----	-----
SWa-L2	DDTMA	0.50	None	-----	-----	-----
SWa-L3	DDTMA	1.00	None	-----	-----	-----
SWa-L1-2	DDTMA	0.25	2	0.1 M	25°C	60
SWa-L1-60	DDTMA	0.25	60	1.0 M	90°C	60
SWa-L2-2	DDTMA	0.50	2	0.1 M	25°C	60
SWa-L2-60	DDTMA	0.50	60	1.0 M	90°C	60
SWa-L3-2	DDTMA	1.00	2	0.1 M	25°C	60
SWa-L3-60	DDTMA	1.00	60	1.0 M	90°C	60
SWa-O1	ODTMA	0.25	None	-----	-----	-----
SWa-O2	ODTMA	0.50	None	-----	-----	-----
SWa-O3	ODTMA	1.00	None	-----	-----	-----
SWa-O1-2	ODTMA	0.25	2	0.1 M	25°C	60
SWa-O1-60	ODTMA	0.25	60	1.0 M	90°C	60
SWa-O2-2	ODTMA	0.50	2	0.1 M	25°C	60
SWa-O2-60	ODTMA	0.50	60	1.0 M	90°C	60
SWa-O3-2	ODTMA	1.00	2	0.1 M	25°C	60
SWa-O3-60	ODTMA	1.00	60	1.0 M	90°C	60

TMA = Tetramethylammonium

DDTMA = Dodecyltrimethylammonium

ODTMA = Octadecyltrimethylammonium

Table 9. Showing the extents of organic cation exchange and acid treatments for Nontronite (SWa-1) derived samples.

Code	Organic cation (OC)	mg OC / g clay*	Clay acid treated (g)	Volume HCl (ml)	HCl Concn	Reaction Temp.	Acid contact time (minutes)
SAz-0	None	-----		-----	-----	-----	-----
SAz-30L	None	-----	1.0	100	6.0 M	25°C	30
SAz-90L	None	-----	1.0	100	6.0 M	25°C	90
SAz-180L	None	-----	1.0	100	6.0 M	25°C	180
SAz-30H	None	-----	1.0	100	6.0 M	90°C	30
SAz-90H	None	-----	1.0	100	6.0 M	90°C	90
SAz-180H	None	-----	1.0	100	6.0 M	90°C	180
SAz-32-30H	MAG	32	1.0	100	6.0 M	90°C	30
SAz-32-90H	MAG	32	1.0	100	6.0 M	90°C	90
SAz-32-180H	MAG	32	1.0	100	6.0 M	90°C	180
SAz-108-30H	MAG	108	1.0	100	6.0 M	90°C	30
SAz-108-90H	MAG	108	1.0	100	6.0 M	90°C	90
SAz-108-180H	MAG	108	1.0	100	6.0 M	90°C	180
SAz-173-30H	MAG	173	1.0	100	6.0 M	90°C	30
SAz-173-90H	MAG	173	1.0	100	6.0 M	90°C	90
SAz-173-180H	MAG	173	1.0	100	6.0 M	90°C	180

TMA = Tetramethylammonium

MAG = Magnafloc 206

*As found by TG Analysis

Table 10. Showing the extents of organic cation exchange and acid treatments for SAz-1 derived samples.

Code	Organic cation (OC)	mg OC / g clay*	Clay acid treated (g)	Volume HCl (ml)	HCl Concn	Reaction Temp.	Acid contact time (minutes)
SWy-0	None	-----		-----	-----	-----	-----
SWy-30L	None	-----	1.0	100	6.0 M	25°C	30
SWy-90L	None	-----	1.0	100	6.0 M	25°C	90
SWy-180L	None	-----	1.0	100	6.0 M	25°C	180
SWy-30H	None	-----	1.0	100	6.0 M	90°C	30
SWy-90H	None	-----	1.0	100	6.0 M	90°C	90
SWy-180H	None	-----	1.0	100	6.0 M	90°C	180
SWy-17-30H	MAG	17	1.0	100	6.0 M	90°C	30
SWy-17-90H	MAG	17	1.0	100	6.0 M	90°C	90
SWy-17-180H	MAG	17	1.0	100	6.0 M	90°C	180
SWy-128-30H	MAG	128	1.0	100	6.0 M	90°C	30
SWy-128-90H	MAG	128	1.0	100	6.0 M	90°C	90
SWy-128-180H	MAG	128	1.0	100	6.0 M	90°C	180
SWy-135-30H	MAG	135	1.0	100	6.0 M	90°C	30
SWy-135-90H	MAG	135	1.0	100	6.0 M	90°C	90
SWy-135-180H	MAG	135	1.0	100	6.0 M	90°C	180

TMA = Tetramethylammonium

MAG = Magnafloc 206

*As found by TG Analysis

Table 11. Showing the extents of organic cation exchange and acid treatments for SWy-2 derived samples.

organocations are at a high, tilted angle to the layer. This data is in agreement with the findings presented in 5.2.2 for the other organoclays prepared for this thesis.

Sample Designation	JP / Å	ST / Å	SWa-1 / Å
Ca ²⁺	14.9	14.7	14.9
M1, M2, M3	14 +/- 0.2	14 +/- 0.2	14 +/- 0.2
L1, L2	14 +/- 0.2	14 +/- 0.2	14 +/- 0.2
L3	17.8 +/- 0.2	17.8 +/- 0.2	17.8 +/- 0.2
O1	13.9 +/- 0.2	13.9 +/- 0.2	13.9 +/- 0.2
O2	16.1	broad range	14.5
O3	20.1	22.2	21.6

Table 17. d_{001} for the non-acid treated organoclays. This data is provided by the co-workers in Bratislava.

7.2.2 % Carbon Values.

Table 18 shows the % carbon values and the amount of Ca²⁺ displaced for the exchanged JP, ST and SWa-1 clays. (Data is supplied by co-workers and therefore is not available for the SAz-1 and SWy-2 derived samples). This data shows that:

- The amount of organocation adsorbed increased with the amount offered.
- The organocation is absorbed by cation exchange and not intercalation.
- The amount of organocation displaced increased with the severity of acid treatment.
- In general DDTMA⁺ and ODTMA⁺ were more resistant than TMA⁺ to displacement by H⁺.

Sample	% carbon	meq Ca ²⁺ released	Sample	% carbon	Sample	% carbon
JP-M1	1.2	0.23	JP-M1-2	1.2	JP-M1-4	1.2
JP-M2	1.9	0.32	JP-M2-2	ND	JP-M2-4	1.7
JP-M3	2.9	0.53	JP-M3-2	ND	JP-M3-4	2.4
JP-L1	4.9	0.30	JP-L1-2	ND	JP-L1-4	5.1
JP-L2	9.7	0.51	JP-L2-2	ND	JP-L2-4	9.7
JP-L3	15.2	0.82	JP-L3-2	ND	JP-L3-4	13.9
JP-O1	6.4	0.34	JP-O1-2	ND	JP-O1-4	6.7
JP-O2	12.9	0.54	JP-O2-2	ND	JP-O2-4	13.3
JP-O3	22.4	0.87	JP-O3-2	ND	JP-O3-4	22.5

Sample	% carbon	meq Ca ²⁺ released	Sample	% carbon	Sample	% carbon
ST-M1	1.0	0.15	ST-M1-2	ND	ST-M1-60	0.6
ST-M2	1.6	0.26	ST-M2-2	ND	ST-M2-60	0.9
ST-M3	2.0	0.31	ST-M3-2	ND	ST-M3-60	0.9
ST-L1	4.9	0.27	ST-L1-2	5.3	ST-L1-60	5.1
ST-L2	9.2	0.48	ST-L2-2	ND	ST-L2-60	8.4
ST-L3	13.6	0.74	ST-L3-2	ND	ST-L3-60	10.7
ST-O1	6.4	0.27	ST-O1-2	6.7	ST-O1-60	6.9
ST-O2	ND	0.49	ST-O2-2	ND	ST-O2-60	ND
ST-O3	ND	0.81	ST-O3-2	ND	ST-O3-60	13.2

Table 18. Showing % carbon values and meq Ca²⁺ released. Sample designations are given in Tables 7 - 11
 This data is provided by the co-workers in Bratislava.

Sample	% carbon	meq Ca ²⁺ released	Sample	% carbon	Sample	% carbon
SWa-M1	1.2	0.18	SWa-M1-2	ND	SWa-M1-60	0.7
SWa-M2	1.7	0.27	SWa-M2-2	ND	SWa-M2-60	0.8
SWa-M3	2.3	0.39	SWa-M3-2	ND	SWa-M3-60	0.9
SWa-L1	4.9	0.28	SWa-L1-2	ND	SWa-L1-60	6.0
SWa-L2	9.5	0.51	SWa-L2-2	ND	SWa-L2-60	8.5
SWa-L3	14.6	0.77	SWa-L3-2	ND	SWa-L3-60	9.4
SWa-O1	6.4	0.28	SWa-O1-2	ND	SWa-O1-60	8.7
SWa-O2	ND	0.49	SWa-O2-2	ND	SWa-O2-60	15.2
SWa-O3	ND	0.83	SWa-O3-2	ND	SWa-O3-60	24.4

Table 18. Continued.

- TMA⁺ ions remained following the maximum acid treatment used. The amount remaining was in excess of that anticipated.

7.2.3 FTIR Analysis.

FTIR spectra of the samples derived from JP, ST and SWa-1 were provided by the co-workers in Bratislava, whilst FTIR spectra for samples derived from SAz-1 and SWy-2 were obtained by the author.

Figure 37 shows untreated JP and JP exchanged with (i) TMA⁺ (JP-M3), (ii) DDTMA⁺ (JP-L3), and (iii) ODTMA⁺ (JP-O3) cations. It can be seen that the bands at 2923 and 2851 cm⁻¹ (asymmetric CH₂ stretch and symmetric CH₂ stretch) are of a higher intensity for JP-L3 and JP-O3 samples than for JP-M3 which is due to the greater number of CH bonds in the alkyl chains. The band at 1488 cm⁻¹ (asymmetric C-H bend in (CH₃)₄N⁺) is characteristic of the TMA⁺ cation (JP-M3). For JP-L3 and JP-O3 this band is replaced by a doublet at 1488 and 1473 cm⁻¹ ((CH₂)_n-deformation). In the spectra of JP, JP-O1, JP-O2, JP-O3 (not shown), there is a gradual decrease in intensity of a water band near 3440 cm⁻¹ together with an increase in intensity of C-H stretching bands at 2923 and 2851 cm⁻¹ from JP, through JP-O1 to JP-O3 which confirmed that the amount of organocation adsorbed increased with the amount offered, as shown by the % carbon values (7.2.2). Interlayer water was displaced by the organocations, which is in agreement with the increasing hydrophobic character of the samples as the organocation content increased.

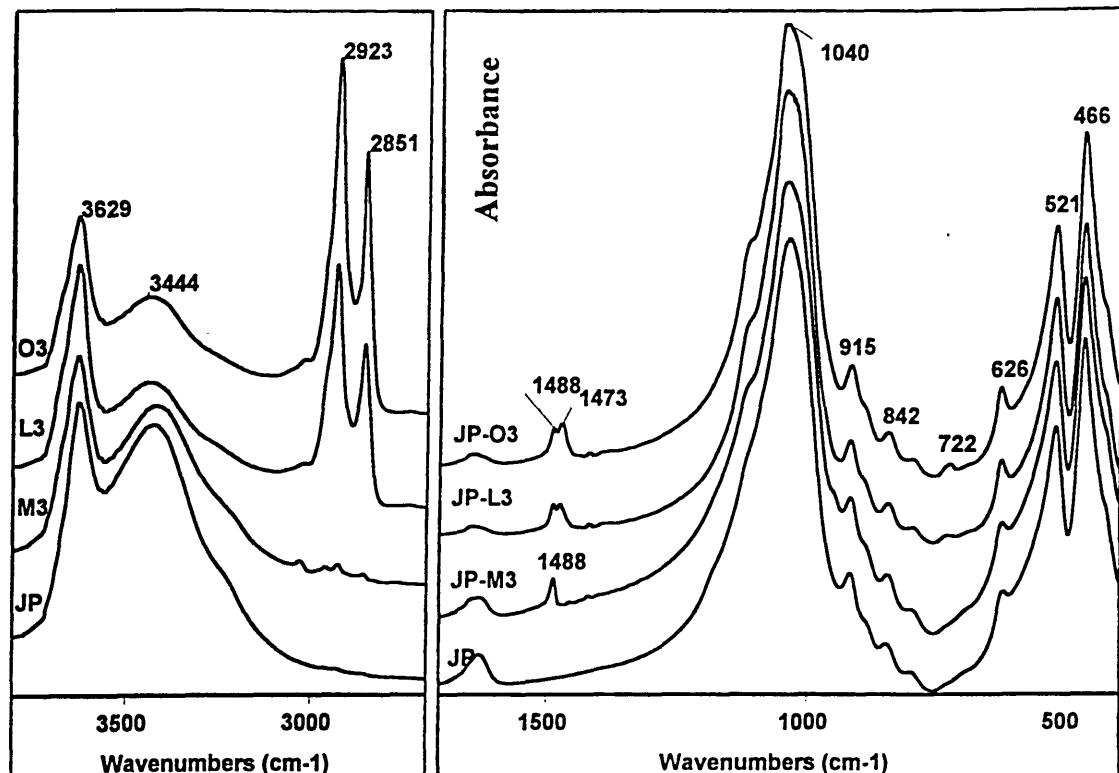


Figure 37. Showing the FTIR spectra of JP, JP-M3, JP-L3 and JP-O3.

The decreasing intensity of the C-H deformation bands reflect the displacement of alkylammonium cations by H⁺ during the course of acid treatment. The intensities of C-H deformation bands for JP-M3-4 and JP-L3-4 (not shown) decreased only slightly compared to those for untreated samples confirming that the mild acid treatment (4 ml, 0.1 M at 25°C) used for JP samples resulted in little organocation displacement. The change in intensity of the CH₃ and CH₂ deformation bands in ST and SWa samples (not shown) were more pronounced. The band at 1488 cm⁻¹ which was clearly evident in ST-M3 and SWa-M3, diminished greatly in intensity for ST-M3-60 and was

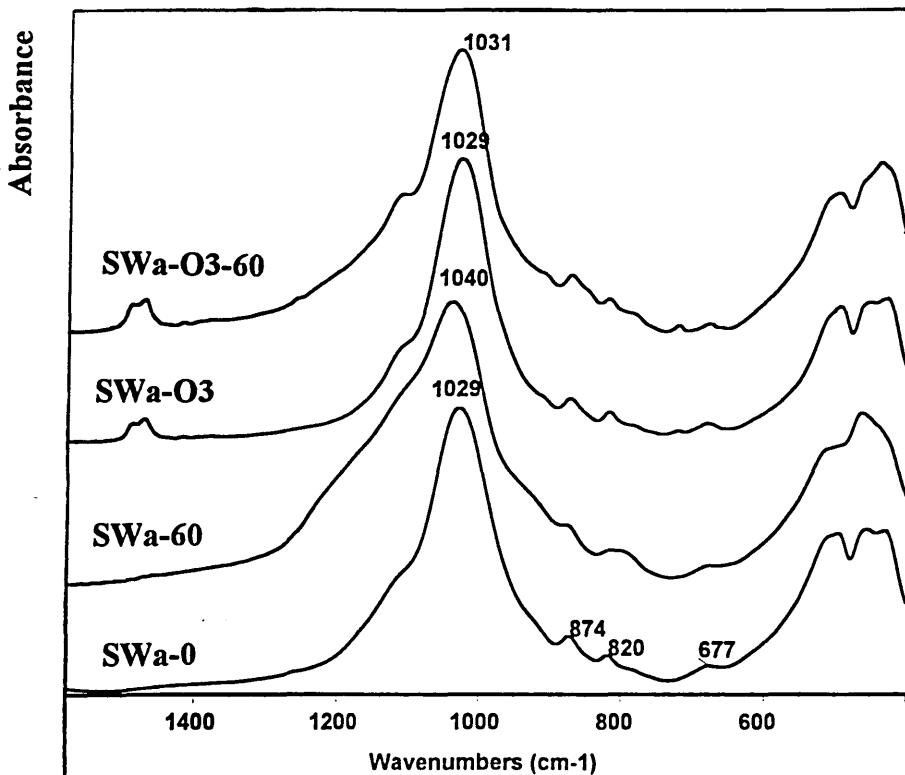


Figure 38. FTIR spectra showing the effect of acid leaching on SWa-1 and SW-O3-60.

only just discernible in SWa-M3-60. In contrast the C-H deformation bands in ST-L3-60 decreased only slightly and were halved in SWa-L3-60. These observations are again in agreement with the % carbon values (7.2.2) and indicate that though the conditions of acid treatment were the same for ST-M3 and ST-L3 as well as for SWa-M3 and SWa-L3, the longer chain alkylammonium ions (DDTMA⁺ and ODTMA⁺) were more resistant to displacement by H⁺ than TMA⁺.

The skeletal vibrations of the clay layer reflect the composition of the octahedral sheet and therefore the extent to which it is depopulated by acid leaching. Acid treatment leads to marked changes in the bands of CH₃ and CH₂, but the band near 1030 cm⁻¹ is

also a significant indicator^{218,219}. Upward shifts of this band (which occurs at 1039 cm⁻¹, 1032 cm⁻¹ and 1029 cm⁻¹ for JP, ST and SWa-1 respectively), would indicate that the octahedral sheet has undergone some dissolution. The band position for all JP and ST samples (not shown), were essentially the same and were not influenced by the resident alkylammonium cation or the extent of acid treatment. However, the shift from 1029 cm⁻¹ in SWa to 1040 cm⁻¹ in SWa-60 (Figure 38), indicated that the hot acid treatment had attacked the clay structure²⁹⁴. A similar shift was observed for SWa-M3-60 (not shown), which again suggested significant depopulation of the octahedral sheet. Conversely, the small shift in this Si-O band for SWa-O3-60 (Figure 38), (and SWa-L3-60, not shown), to 1031 cm⁻¹ suggested minimal depopulation of the octahedral sheet. This is in agreement with the % carbon values (7.2.2) which indicate that a small amount of the adsorbed alkylammonium ions are displaced during acid-activation, although it appears that the remaining longer chain alkylammonium cations protect the clay from acid attack. This may be a result of two factors which affect the accessibility of the interlayer space.

1. Organoclays have a limited ability to swell in aqueous media.
2. The organic cations in the interlayer prevent ingress of protons which would attack sites of isomorphous substitution.

Negligible shift of the Si-O band was also observed for SAz-1 (Figure 39) and SWy-2 (not shown) catalysts prepared by the competitive approach, even under the most concentrated acid conditions. This indicates minimal depopulation of the octahedral shift although there was some reduction in the intensity (by 41%) of the band at 1489

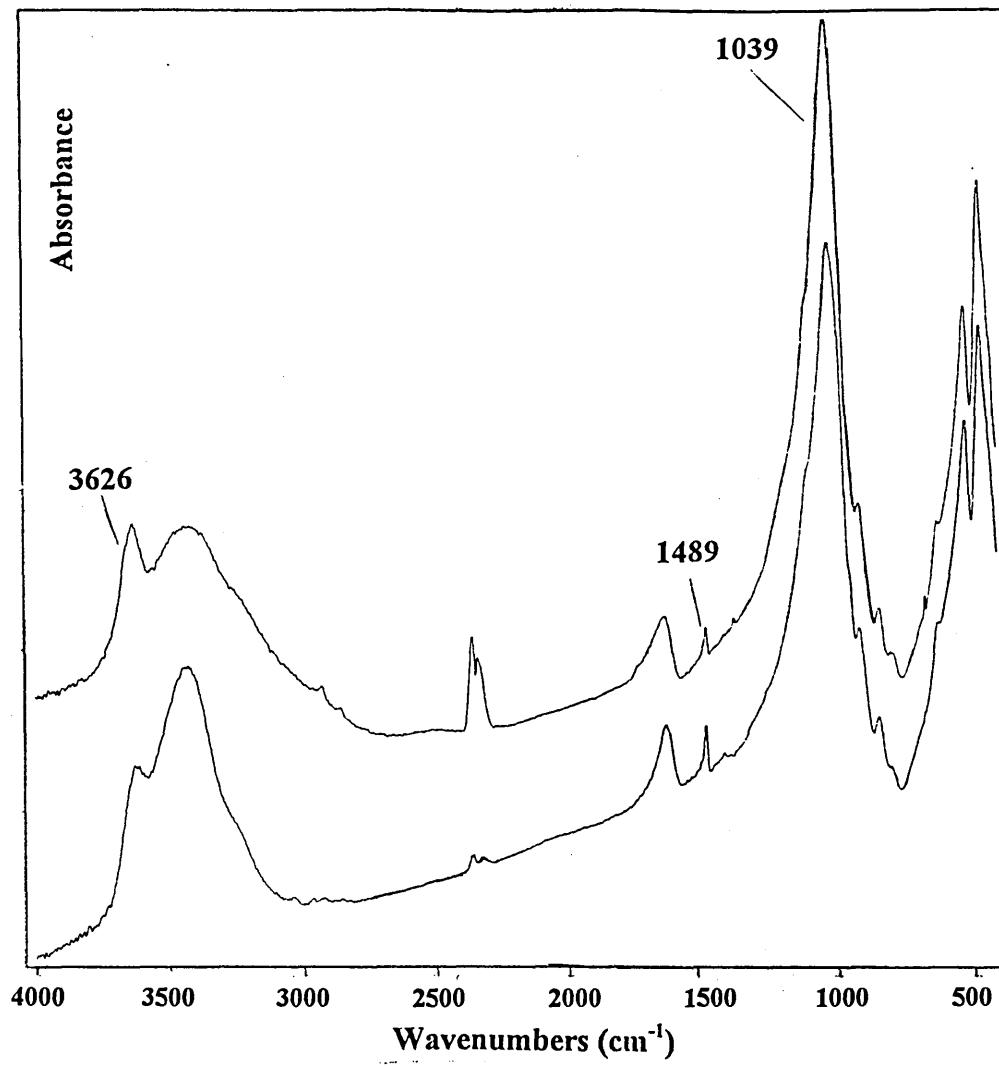


Figure 39. The FTIR spectra of catalysts derived from SAz-1 by the competitive adsorption of a. 1.2 mmol TMA⁺ and 0 mmol H⁺/g clay, b. 1.2 mmol TMA⁺ and 120 mmol H⁺/g clay.

cm⁻¹ (asymmetric C-H bend in (CH₃)₄N⁺) (Figure 39) showing some loss of TMA⁺ cations.

7.2.4 XRF of Acid-Activated Organoclays.

Table 19 shows XRF data obtained for some acid-activated organoclays with data for the base clays shown for comparison. It can be seen that acid-activation has significantly

Oxide	Catalysts prepared by competitive adsorption of TMA ⁺ and H ⁺							
	SAZ-1 + 1.2 mmol TMA ⁺ + x mmol H ⁺				SWy-2 + 0.86 mmol TMA ⁺ + x mmol H ⁺			
SAZ-1	SWy-2	SA-32 -90H*	SWy-17 -90H*	x = 0	x = 32	x = 64	x = 120	
SiO ₂	67.72	68.48	70.85	71.16	69.42	70.80	70.99	71.14
Al ₂ O ₃	19.74	20.16	19.94	21.07	19.86	19.83	19.70	20.81
MgO	7.24	2.77	6.94	2.49	7.08	6.95	6.85	6.82
Fe ₂ O ₃	1.59	4.63	1.81	4.37	2.02	1.78	1.88	1.74
TiO ₂	0.27	0.09	0.26	0.15	0.25	0.26	0.25	0.25
CaO	3.16	1.76	0.04	0.05	1.15	0.21	0.19	0.18
Na ₂ O	0.07	1.70	0.07	0.24	0.10	0.07	0.06	0.08
K ₂ O	0.21	0.41	0.09	0.47	0.12	0.10	0.10	0.09
CsO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	100	100	100	100	100	100	100	100

* Sample designations are shown in Tables 10 and 11.

Table 19. XRF data showing the elemental composition of the acid-activated organoclays. Values for the base clays are shown for comparison. Only the major oxides are shown. Values are as % total weight.

reduced the values for CaO content of both SAz-1 and SWy-2 derived samples, showing that the resident cations were replaced by protons, organocation and/or polycation. Similarly, there is a decrease in Fe₂O₃ and MgO content suggesting there is an amount of acid leaching. That this is not apparent from the Si-O band in the FTIR data supports the observation that the lattice is not extensively destroyed. The Al₂O₃ content does not vary significantly as might be expected by the decrease in MgO content, since displaced Al³⁺ is more readily readSORBED on the exchange sites during autotransformation compared to Mg²⁺²²⁹.

7.3 THE CATALYTIC CONVERSION OF α -PINENE.

As discussed in Section 3.13.3, α -pinene reacts readily in acids by either ring expansion or ring opening. Ring expansion favours the production of camphene (by shift of the gem-dimethyl bridge), or α -fenchene (by shift of the methylene bridge), whilst ρ -menthadienes (including limonene, terpinolene and α -terpinene) are favoured by ring opening.

Specifically, camphene results from the ion shown in Figure 40a by elimination and simultaneous bond shift. Elimination is initiated by proton loss from C-10, from which two possible rearrangements are open. Displacement of the partial bond from C-2 to C-7 yields β -pinene. Alternatively, shift of the electrons of the (C-2)-(C-3) bond to give a bond between C-3 and C-1, displaces the partial bond between C-1 and C-7. A bond remains between C-2 and C-7 which results in the structure shown in Figure 40b which is camphene²⁷⁵. Other possible mechanisms are ruled out since the products of those mechanisms were not found by Williams *et al.*²⁷⁵ or herein.

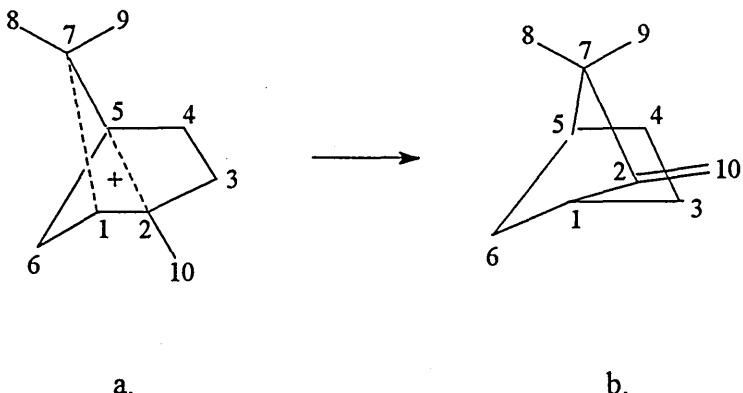


Figure 40. Showing the Mechanism for the Formation of Camphene.

The products obtained for the reactions performed herein were identified by GC-MS with the amounts being determined by separate GC analysis. The significant products were found to be camphene and limonene with minor amounts of other products, the predominant one being *i*-terpinolene.

The percentages yields of camphene, limonene and other products from catalysts derived from JP, SWa-1 and ST are given in Figure 41 where they are together for ease of comparison. Expanded versions are given later in Figures 42 - 44 to enable more detailed observations. The overall trends are very similar with few extreme differences and are summarised below.

- The most effective catalysts were those derived from TMA⁺ exchanged smectites.
- The acid-activated TMA⁺ exchanged smectites gave total conversions of between 60 and 90%.
- Catalysts derived from smectites exchanged with small amounts of the longer chain organocations, DDTMA⁺ and ODTMA⁺ gave appreciable conversions. Those

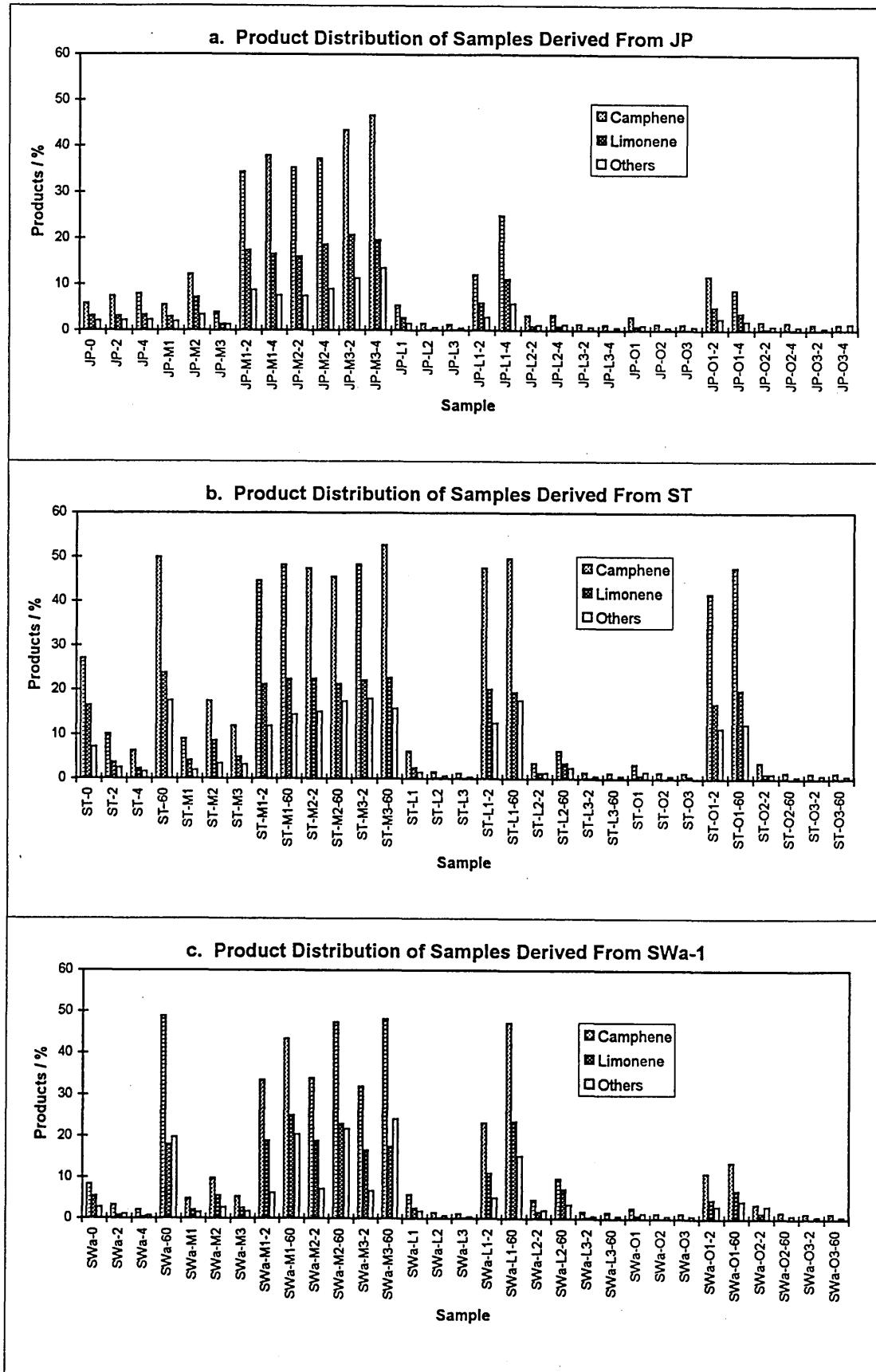


Figure 41. Showing the product distribution of samples derived from a. JP, b. ST, and c. SWa-1.

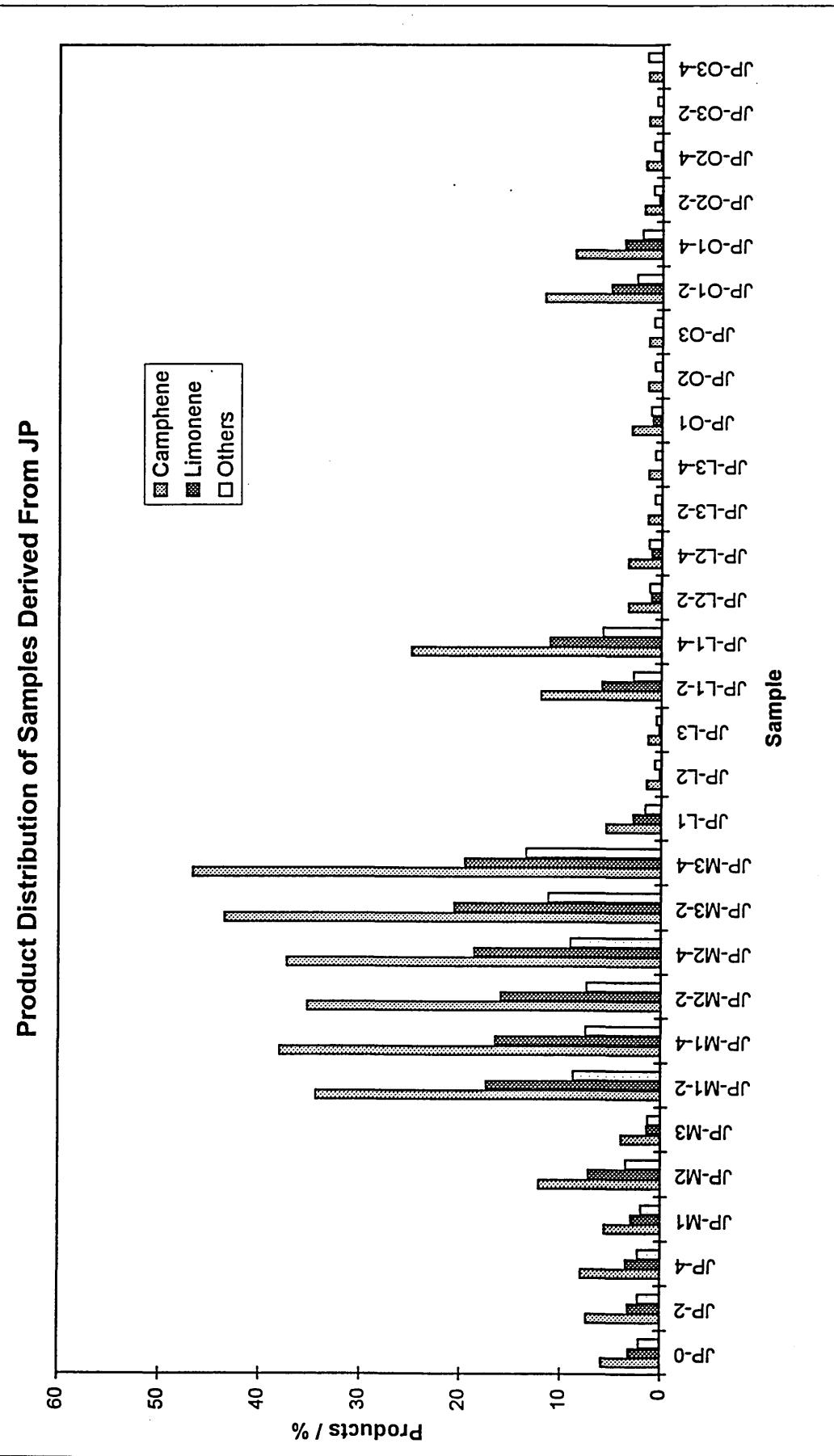


Figure 42. Showing the product distribution of samples derived from JP.

derived from ST (i.e. ST-L1-2, ST-L1-60, ST-O1-2 and ST-O1-60), gave conversions comparable to the acid-activated TMA⁺ exchanged ST samples.

There are a number of key observations regarding the results obtained from samples derived from the different types of clay. The points of note from the results obtained for JP derived samples (Figure 42) are summarised below in point form for clarity.

- The acid treated base clays (JP-2 and JP-4), did not produce large amounts of camphene and limonene.
- When 50% of the resident Ca²⁺ cations were replaced with TMA⁺ (JP-M2), the yields were increased.
- Mild acid treatment of samples exchanged with TMA⁺ cations (JP-M1-2, JP-M1-4, JP-M2-2, JP-M2-4, JP-M3-2, JP-M3-4), increased the yield by a factor of four.
- This fourfold increase in yield showed little dependence on the amount of TMA⁺ cations present. Samples containing small amounts of TMA⁺ cations (e.g. JP-M1-2), were as effective as those containing large amounts (e.g. JP-M3-2).
- The increase in yield upon acid treating both DDTMA⁺ and ODTMA⁺ containing samples was of the same order (c.f. JP-L1 and JP-L1-4), as that seen for the TMA⁺ containing samples. The effect is less striking since the non-acid treated, longer chain organoclays (e.g. JP-L2), showed minimal activity in the first instance.

Points of note from the results obtained for ST derived samples (Figure 43) are similarly summarised below.

- Untreated ST gave a surprisingly high yield compared to the other untreated clays.

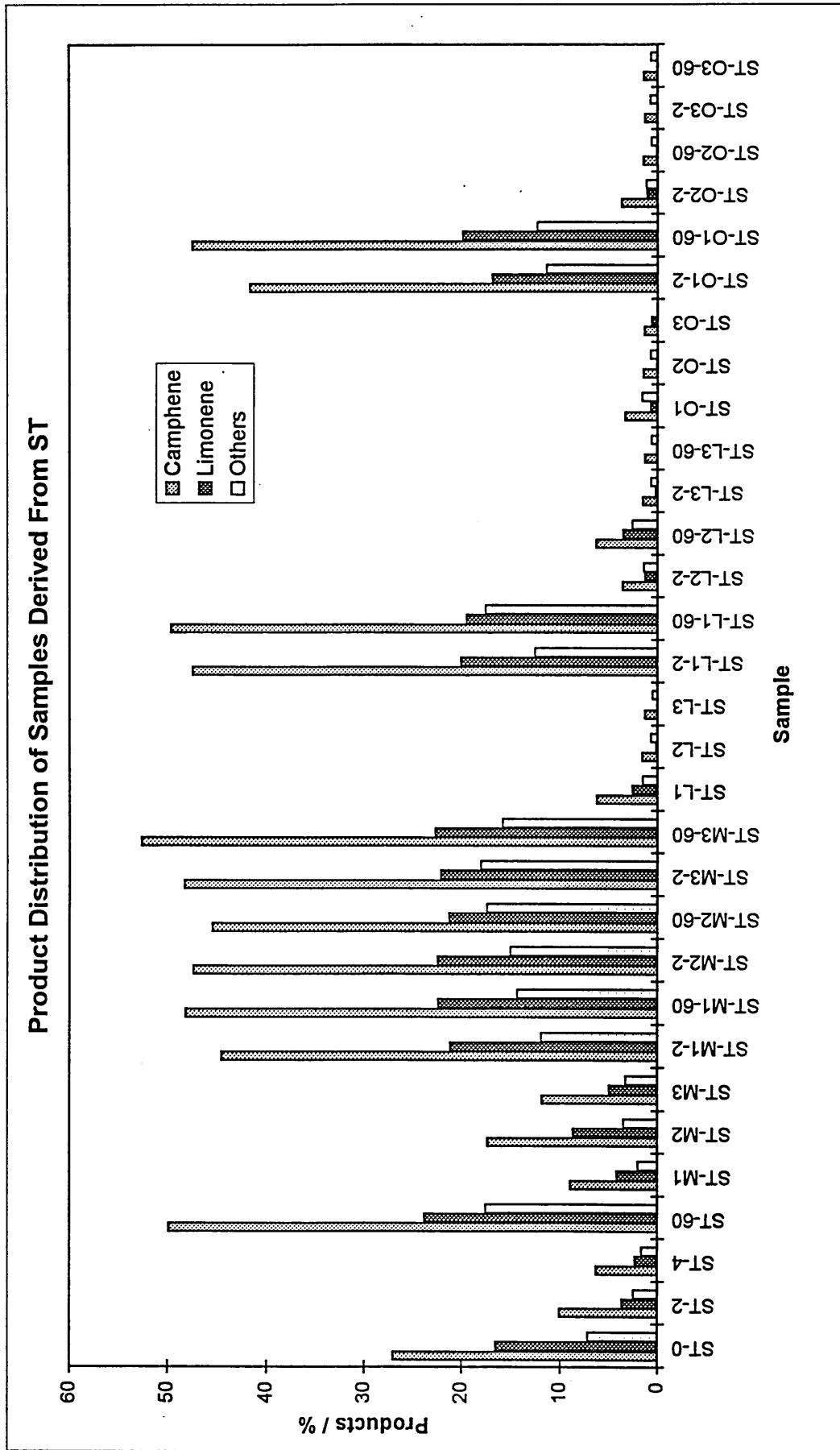


Figure 43. Showing the product distribution of samples derived from ST.

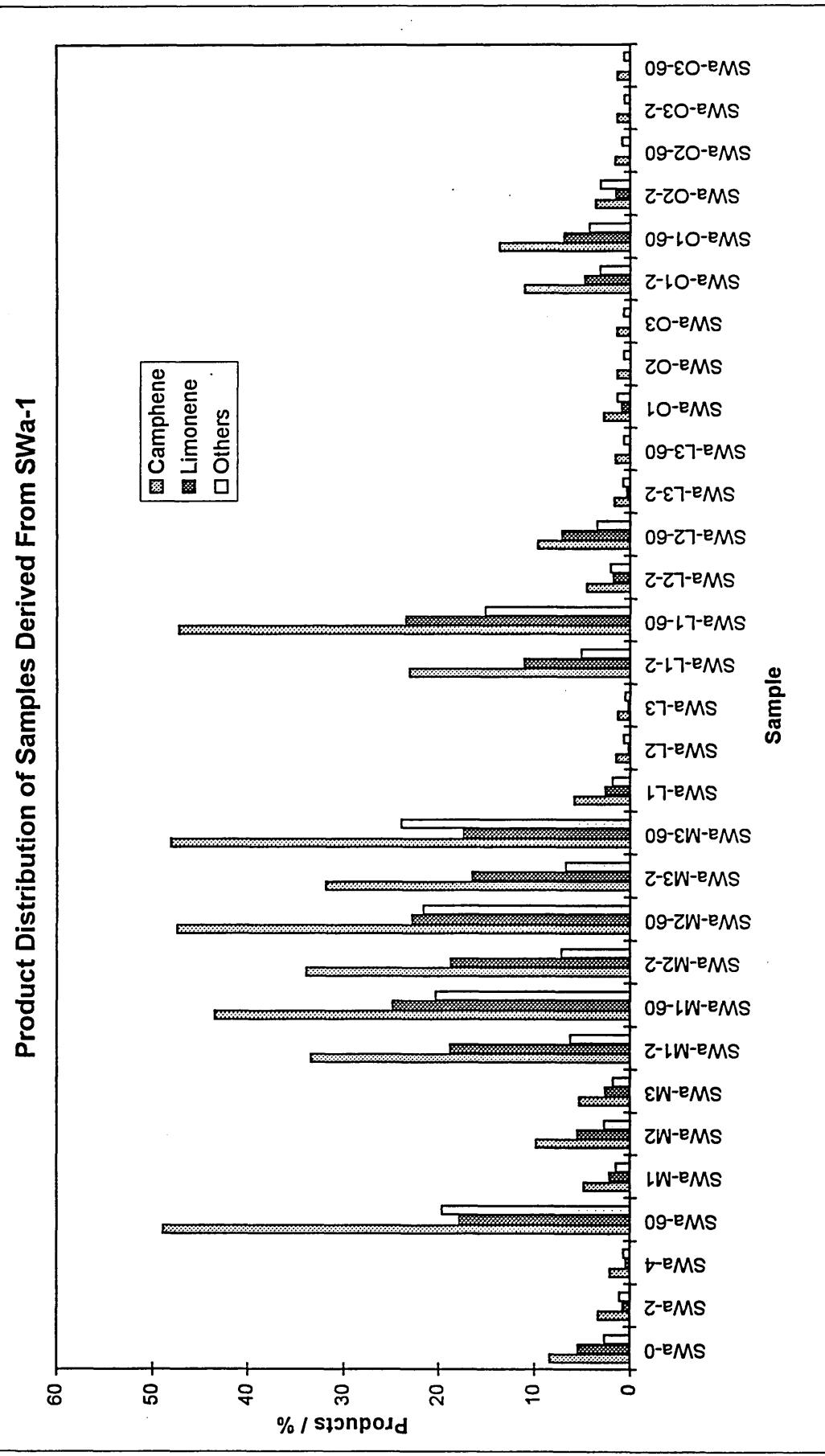


Figure 44. Showing the product distribution of samples derived from SWa-1.

- Mild acid treatment (2 or 4 ml of 0.1 M HCl), reduced the observed activity of untreated ST.
- Harsh acid treatment (60 ml of 0.1 M HCl, 25°C), significantly enhanced the activity of the ST base clay.
- Acid treatment of ST-M1, ST-M2 and ST-M3 did not enhance the yield as compared to ST-60.
- Yields obtained from ST-L1-2, ST-L1-60, ST-O1-2 and ST-O1-60 were equal to those obtained from acid treated TMA⁺ containing samples.
- Acid treated samples exchanged with 50 or 100% DDTMA⁺ or ODTMA⁺ cations gave minimal yields.

The points of note from the results obtained for SWa-1 derived samples (Figure 44) are summarised below.

- Severe acid treatment of the base smectite (60 ml of 1 M HCl, 95°C, SW-60) produced activity equivalent to the acid treated TMA⁺ exchanged smectite.
- As with JP-M2 and ST-M2, the yield for the untreated 50% TMA⁺ exchanged smectite exceeded that of those containing nominally 25 or 100% of the CEC.
- There was a decrease in yield (although still appreciable), for TMA⁺ exchanged SWa treated with 2 ml of 0.1 M HCl at 25°C (e.g. SWa-M1-2) compared to those treated with 60 ml of 1.0 M HCl at 95°C (e.g. SWa-M1-60).
- The decrease in yield noted for the TMA⁺ exchanged ST catalysts with mild and harsh acid treatments was even more marked for SWa-L1-2 and SWa-L1-60.

- Yields obtained from SWa-O1-2 and SWa-O1-60 were similar to the corresponding JP catalysts, JP-O1-2 and JP-O1-4.

The high activity of SWa-60 was expected because of the large quantity of iron present in the tetrahedral and octahedral layers, which is more easily leached than aluminium under such conditions²⁹⁴. This catalyst is comparable with the catalysts prepared by Rhodes and Brown²⁷⁰ in that the extensively leached clay exhibits appreciable hydrophobicity.

Using the formation of tetrahydropyranyl ether from dihydropyran and methanol as a test reaction Rhodes and Brown²⁷⁰ established that the catalytic activity of acid-activated clay for reactions in polar media was optimised when the acidity and swelling ability of the catalyst was at a maximum. This occurred at short acid treatment times. In contrast, the yield for the acid catalysed isomerisation of α -pinene to camphene, which represents reaction in a non-polar medium, was optimised when the external surface area reached a maximum, which occurred when leaching was extensive. They concluded that the reaction in polar media was optimised at short acid treatment times because the hydrophilic aluminosilicate surface attracts the polar reagents to the surface where the catalytic protons reside. This contrasts with the behaviour in non-polar media where the reaction yield was optimised when the clay was substantially leached because the catalyst presented an essentially hydrophobic surface which served to attract the non-polar reagents. Their data is, however, limited to the study of a single clay with a high octahedral Al^{3+} content.

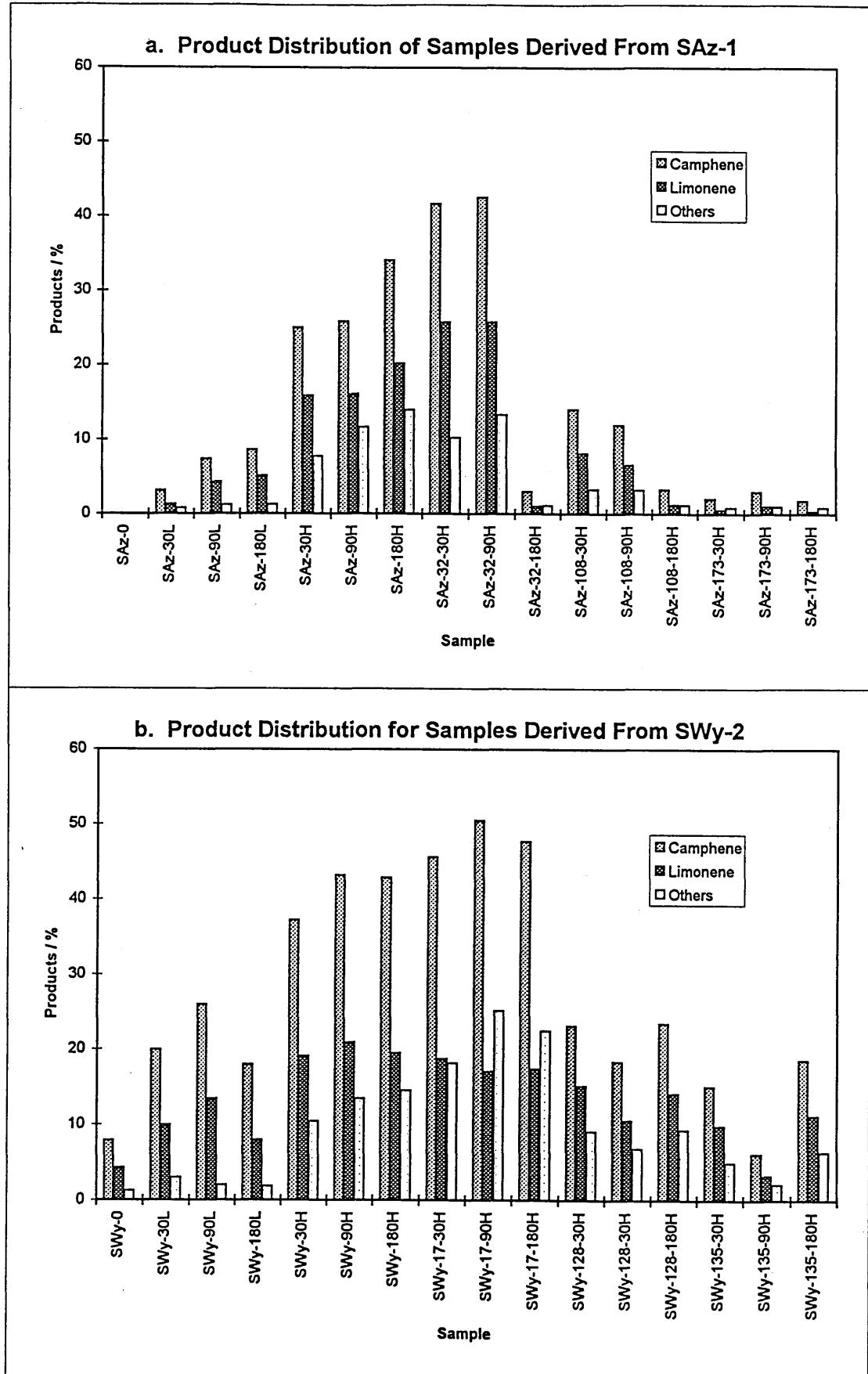


Figure 45. Showing the product distribution for acid-activated, polymer-exchanged a. SAz-1 and b. SWy-2.

Figure 45 shows the product distribution for acid-activated, polymer-exchanged SAz-1 (a) and SWy-2 (b). These samples are not directly comparable to the Slovak samples since the conditions of acid-activation differ, however both the Slovak samples and the samples prepared herein include severe acid treatments. It can be seen that for both SAz-1 and SWy-2 derived samples:

- Acid treatment of the base clays resulted in considerable activity. At maximum acid-activation, 34% (SAz-180H) and 43% (SWy-180H) camphene was produced. This was not as great a conversion as for ST and SWa-1 derived samples (ST-60, Figure 43; SWa-60, Figure 44) which produced \approx 50%, but was still significant.
- In comparison, room temperature acid treatment of SAz-1 for 180 minutes (SAz-180L) increased production of camphene from zero to 9% whilst room temperature acid treatment of SWy-1 for 180 minutes (SWy-180L) increased production from 8 to 18%.
- In general, the presence of low loadings of polymer (e.g. SAz-32-30H which contains 32 mg polymer/g clay, and SWy-17-30H which contains 17 mg polymer/g clay), resulted in maximum yields of camphene.
- The maximum yield for SAz-1 derived samples was 43% (SAz-32-90H) and for SWy-2 derived samples was 51% (SWy-17-90H).
- Maximum yields for both SAz-1 and SWy-2 derived samples were obtained for acid-activation of 90 minutes duration.
- Increasing the loading of polymer decreases the catalyst activity. This was more significant for SAz-1 derived samples than for SWy-2 derived samples. The latter retained considerable activity over a range of polymer loadings.

- Only samples containing a low loading of polymer i.e. those containing the designations SAz-32 or SWy-17, showed enhanced activity compared to the acid-activated base clays (i.e. those containing no polymer).

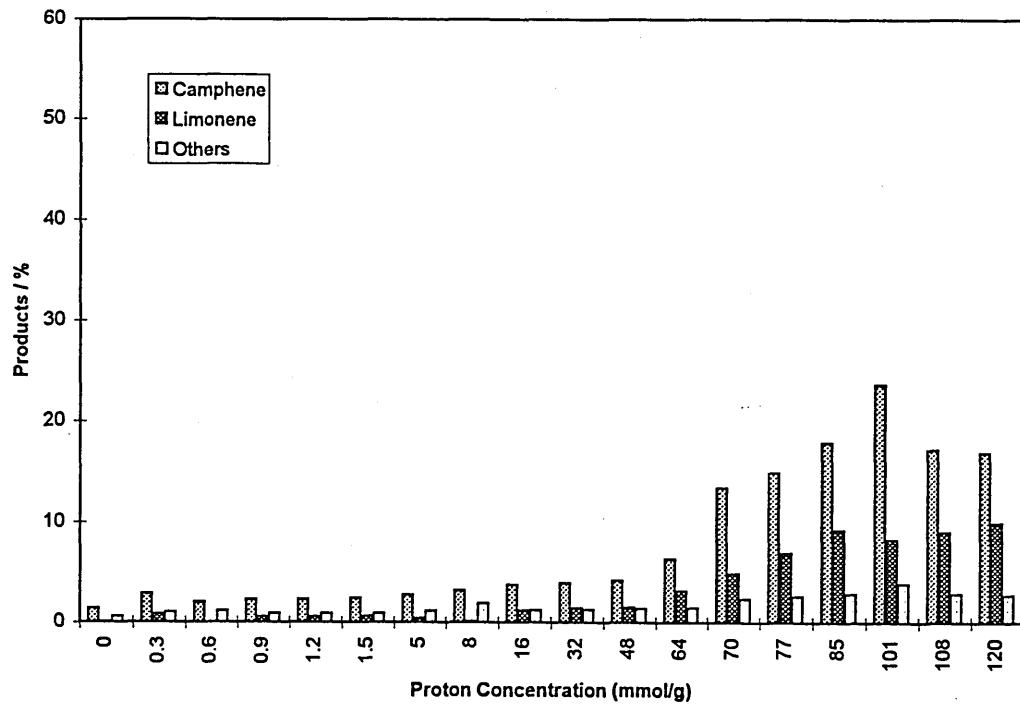
A significant difference in trend between SAz-1 and SWy-2 derived samples was noted for samples containing a low loading of polymer and acid treated for 180 minutes at high temperature (SAz-32-180H = 32 mg polymer/g SAz-1 clay, SWy-17-180H = 17 mg polymer/g SWy-2 clay). The SWy-2 derived sample still showed significant activity (48% camphene) whereas the activity for the SAz-1 derived sample was drastically reduced (3% camphene). This suggests that 180 minutes of acid-activation was sufficient to achieve significant dissolution of the octahedral sheet for SAz-1. This trend was also evident from the samples containing intermediate loadings of polymer i.e. those containing the designations SAz-108 or SWy-128. The activity of SAz-108-180H was significantly reduced compared to SAz-108-90H whereas SWy-128-180H retained significant activity. The trend for the SAz-1 derived samples containing the greatest loading of polymer (173 mg polymer/g clay), i.e. those containing the designation SAz-173, was unclear as all samples showed insignificant activity (< 3% camphene).

Clearly, mild acid treatment of TMA-exchanged samples gave high yields of product regardless of TMA⁺ loading. Whereas clays treated with ODTMA⁺, DDTMA⁺ and polycation showed significant reduction in activity as loading increased. Therefore this work concentrated on TMA-exchanged clay and the balance between TMA⁺ and H⁺. A simple method of sample preparation was also required so the competition between TMA⁺ and H⁺ was investigated.

Figure 46 considers samples prepared by the competitive adsorption approach which combines organic cation exchange with simultaneous acid treatment at room temperature. Figure 46 shows the product distribution for samples derived from SAz-1 (a) and SWy-2 (b). Each type of clay has had the amount of cation offered, as well as the concentration of acid present, adjusted to consider the CEC of the clay. Sufficient TMA⁺ cations are offered to fulfil the CEC in each case, 1.2 mmol TMA⁺/g SAz-1, 0.86 mmol TMA⁺/g SWy-2. A range of acid concentrations from 0 - 120 mmol H⁺/g clay were also offered. Note that the scales on these Figures are non-linear. As is seen for previous methods of sample preparation, samples derived from SWy-2 show enhanced activity compared to those samples derived from SAz-1. However, there are similarities in trends between the two types of clay. It is clear that for each clay there are optimum conditions for the amount of organic cation present and the extent of acid treatment to achieve maximum yield.

Figure 29 (Section 5.2.3) shows that TG analysis can be used to accurately determine the amount of TMA⁺ adsorbed onto a clay. Figure 47 shows percentage camphene produced as a function of total TMA⁺ content of the resultant catalysts, determined using TG analysis, and the strength of acid treatment. It can be seen that there are significant differences between the two types of clay. The first difference is reflected in the shape of the curves concerning TMA⁺ content. That related to SWy-2 (Figure 47b) shows an initial steep loss whereas the curve related to SAz-1 (Figure 47a) is more linear. TMA⁺ cations also appear to be surprisingly resistant to replacement by protons. In previous samples the organoclay (both TMA-SAza-1 and TMA-SWy-2) is first prepared, then acid-activated, yet retains much of its organic content. The competitive adsorption study confirms the resilience of the TMA⁺ cations, i.e. the acidic protons are not totally

a. Product Distribution of Samples Derived From SAz-1 Following Competitive Adsorption of 1.2 mmol TMA/g Clay and Varying Proton Concentrations



b. Product Distribution of Samples Derived From SWy-2 Following Competitive Adsorption of 0.86 mmol TMA/g Clay and Varying Proton Concentrations

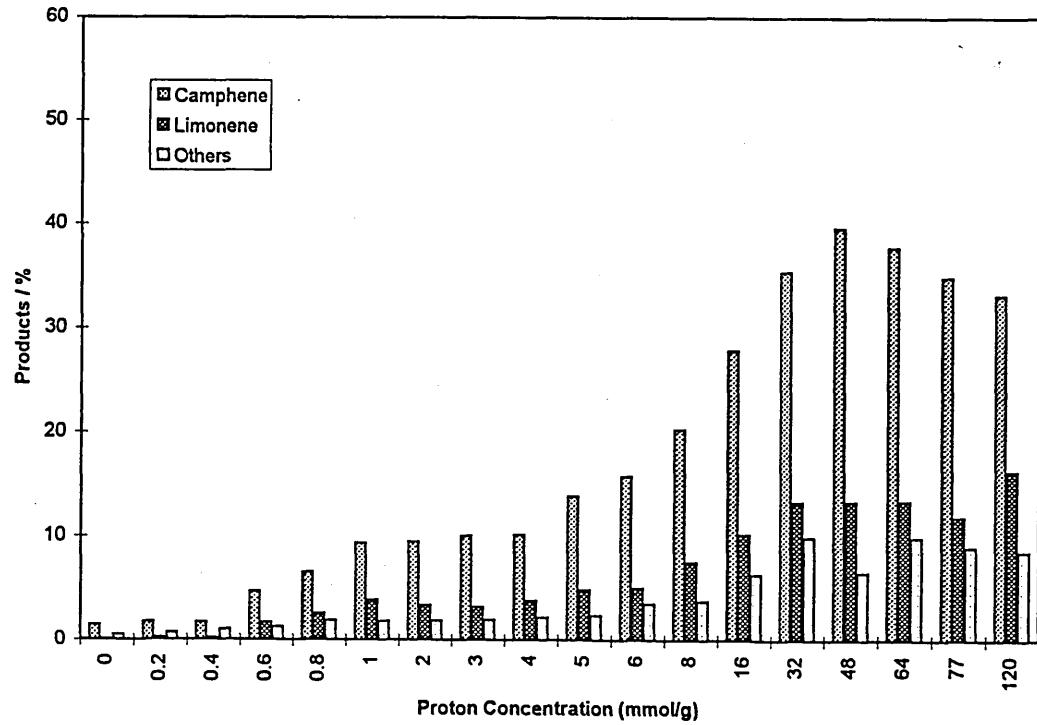


Figure 46. Showing the product distribution of samples prepared by competitive adsorption.

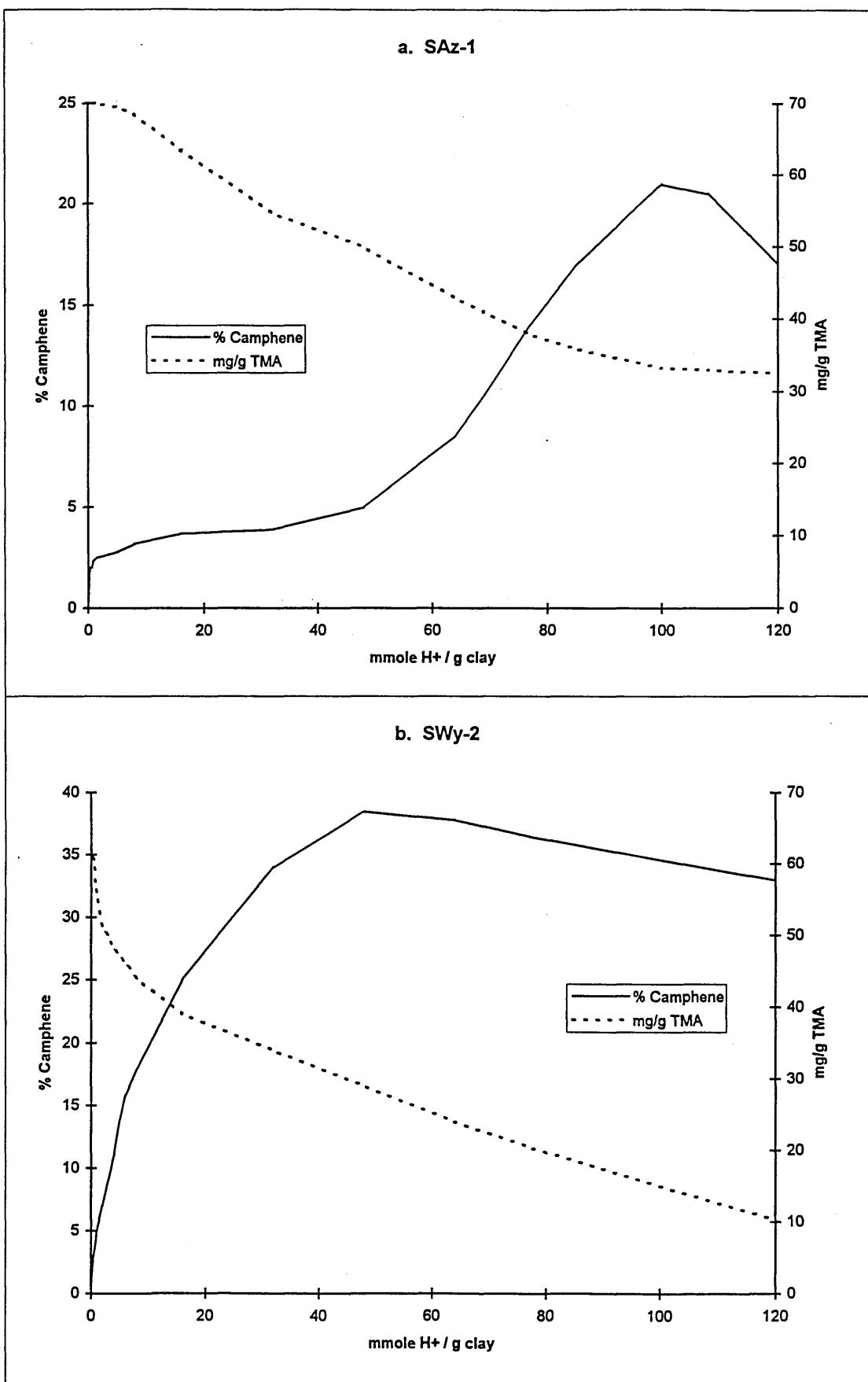


Figure 47. Showing the % camphene produced as a function of TMA^+ content.

displacing the TMA⁺ cations. In fact, for catalysts derived from both types of clay, maximum activity is achieved near 50% loading of TMA⁺.

When comparing the results presented herein with those of other workers it must be considered that each group uses a different method of acid-activation. In general, the total conversions (based on α -pinene) were between 60 and 80% in order of activity, JP = SAz-1 < SWa-1 < ST = SWy-2. These conversions are considerably higher than those reported by Rhodes and Brown²⁷⁰ for extensively acid-leached Texas bentonite, but are similar to results reported by De Stefanis *et al.*²⁷⁸. They²⁷⁸ investigated the reaction of α -pinene in several permanently porous materials including two mid pore zeolites (denoted USY and NH₄⁺-ZSM-5, with SiO₂/Al₂O₃ ratios = 35 and 235), and Al- and Al,Fe-pillared interlayer clays (denoted Al-PILC and FAZA). They carried out their reactions under Lewis acid conditions (i.e. each solid was extensively dehydrated) and for 5 hours duration at 100°C in a sealed glass reactor. These conditions are far more severe than those used in this work and yet De Stefanis *et al.*²⁷⁸ achieved only 42 - 48% conversion of α -pinene to camphene which does not exceed these yields reported herein.

De Stefanis *et al.*²⁷⁸ also found a different level of selectivity. They found that the selectivity of USY and the pillared clays were similar with a camphene : limonene ratio near to three. Figure 48 a-e shows the selectivity of many of the organoclays used herein. The catalysts derived from Slovak clays (Figure 48 a-c) were less selective towards camphene with a ratio of 2.2:1. The polymer containing SAz-1 and SWy-2 derived catalysts (Figure 48 d-e) were less selective again with a ratio near 2:1, although selectivity was more erratic for samples derived from SAz-1 than for those derived from SWy-2. The catalysts prepared by competitive adsorption exhibit selectivities (not

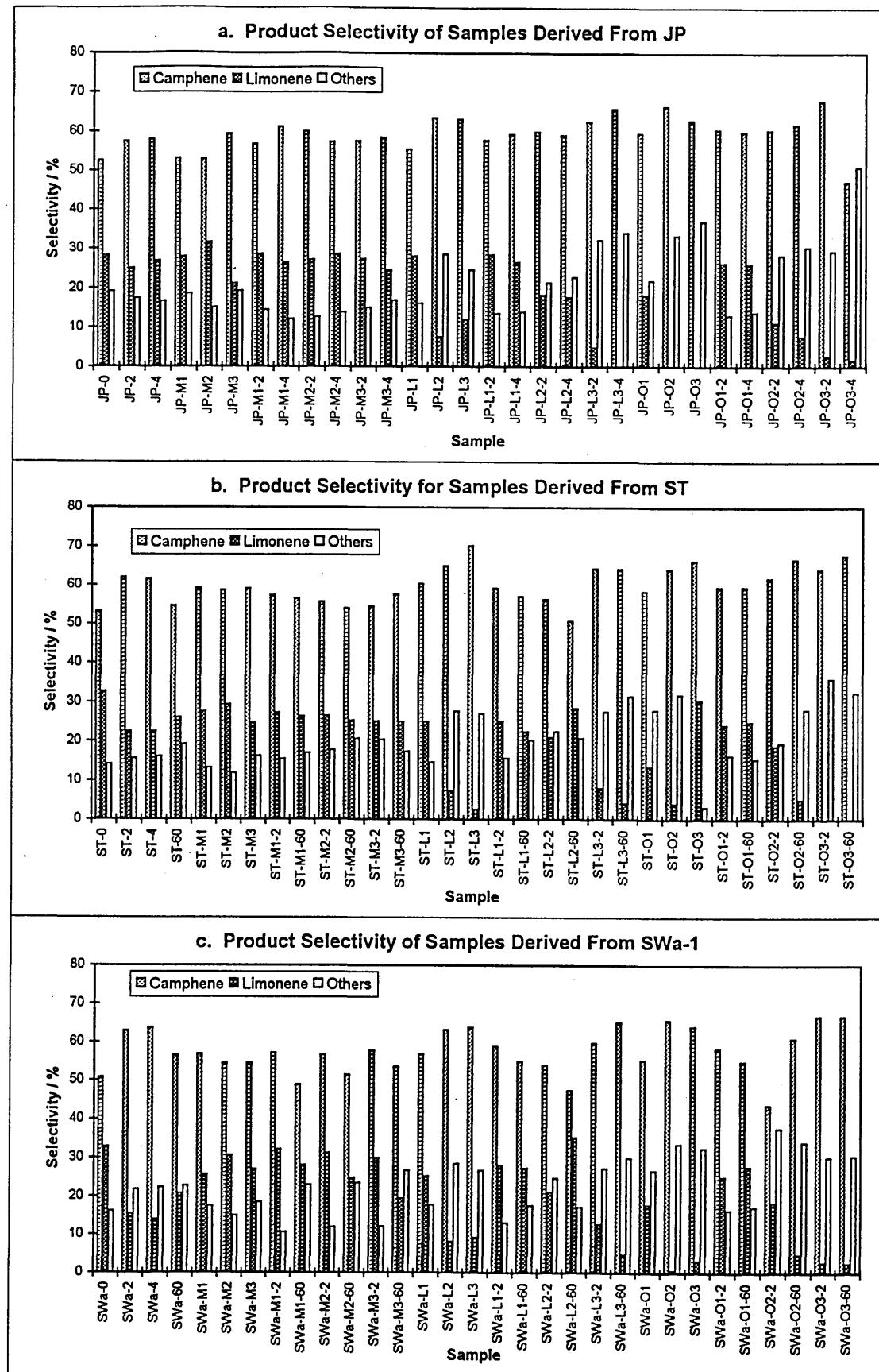


Figure 48. Showing the product selectivities of the acid-activated organoclays.

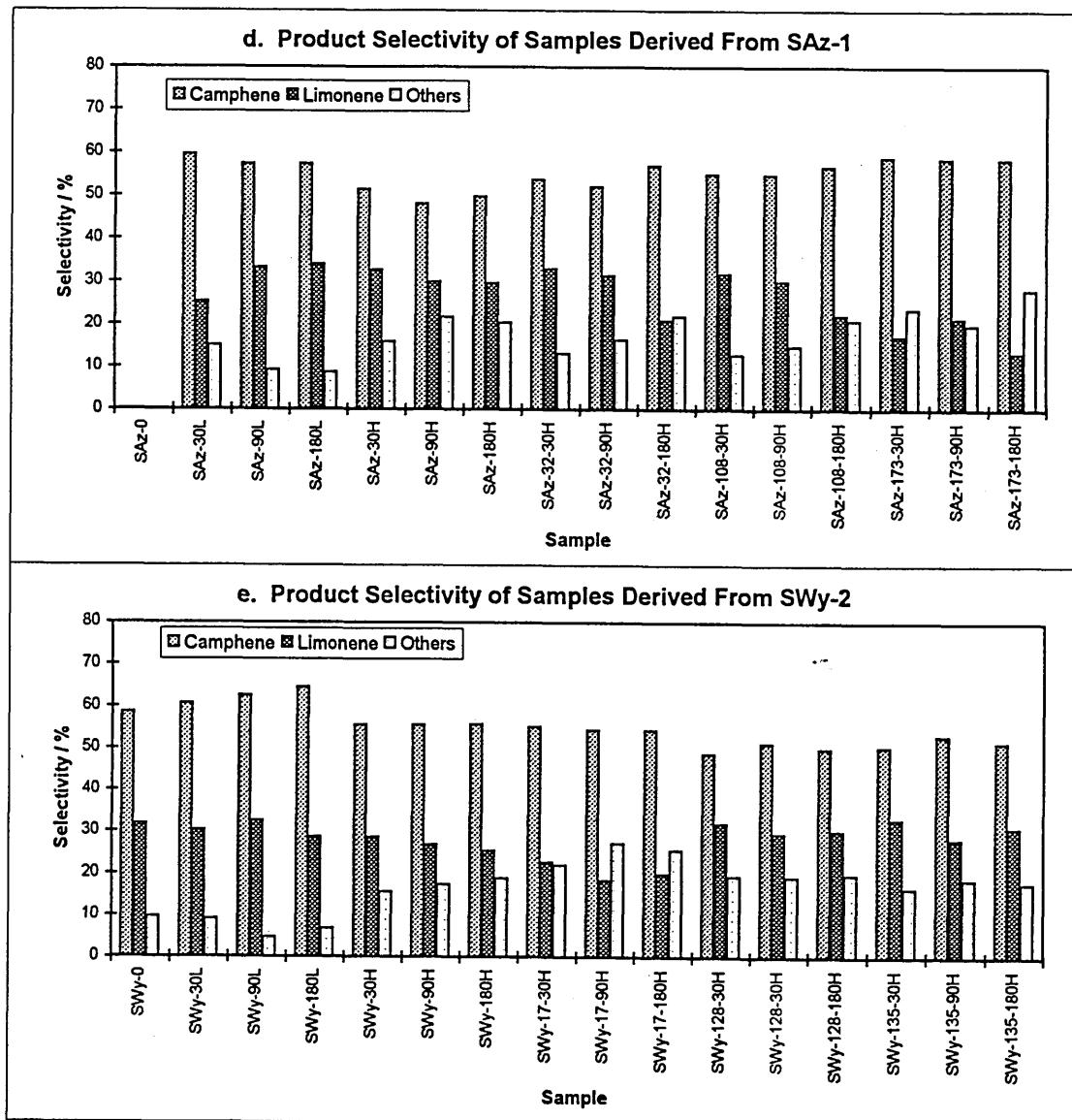


Figure 48. Continued.

shown) similar to the catalysts derived from Slovak clays, i.e. 2.2:1. In general the yield appears to be controlled by the reaction temperature of 80°C. These selectivities may reflect the swelling ability of the clays in the reaction medium.

Kullaj²⁹⁶ reported that when α -pinene is heated with bentonite treated with 10% HCl the products are camphene and tricyclene, which led De Stefanis *et al.*²⁷⁸ to suggest that the absence of tricyclene amongst the products derived from USY and PILCs indicated that the reactions were taking place within the pore network. The fixed, porous nature of USY and the PILCs mean that they are unable to swell and therefore may select against the size of the limonene molecule. This is less likely with the catalysts derived from alkyltrimethylammonium-clays because the charge balancing organocations do not bind the layers together as the alumina pillars do in PILCs and thus these organoclays can avail of their ability to expand in the reaction liquor. Similarly, catalysts containing low loadings of polymer (i.e. those containing the designations SAz-32 and SWy-17), will retain their ability to swell in water and allow proton attack on the silicate surface during acid activation. Increasing loadings of polymer hold the clay layers more firmly together, thus reducing their swelling ability and hence the ease of proton attack on the silicate surface. Therefore high polymer loadings ultimately reduce catalytic activity (as seen previously in Figure 45). This relationship between polymer loading and the ability of a clay to swell in solvents has also been observed by Billingham *et al.*²⁸⁵. At low loadings the x-ray diffraction trace of polycation-exchanged SWy-2 (after immersion in an aqueous dispersion containing 3% polyethylene glycol), contained peaks which could be attributed to polycation expanded layers (15.2 Å), and layers expanded by a bilayer of polyethylene glycol (18.4 Å). At polycation loadings of > 0.6 CEC only the 15.2 Å

Product Distribution of Minerals With Varying Iron Content

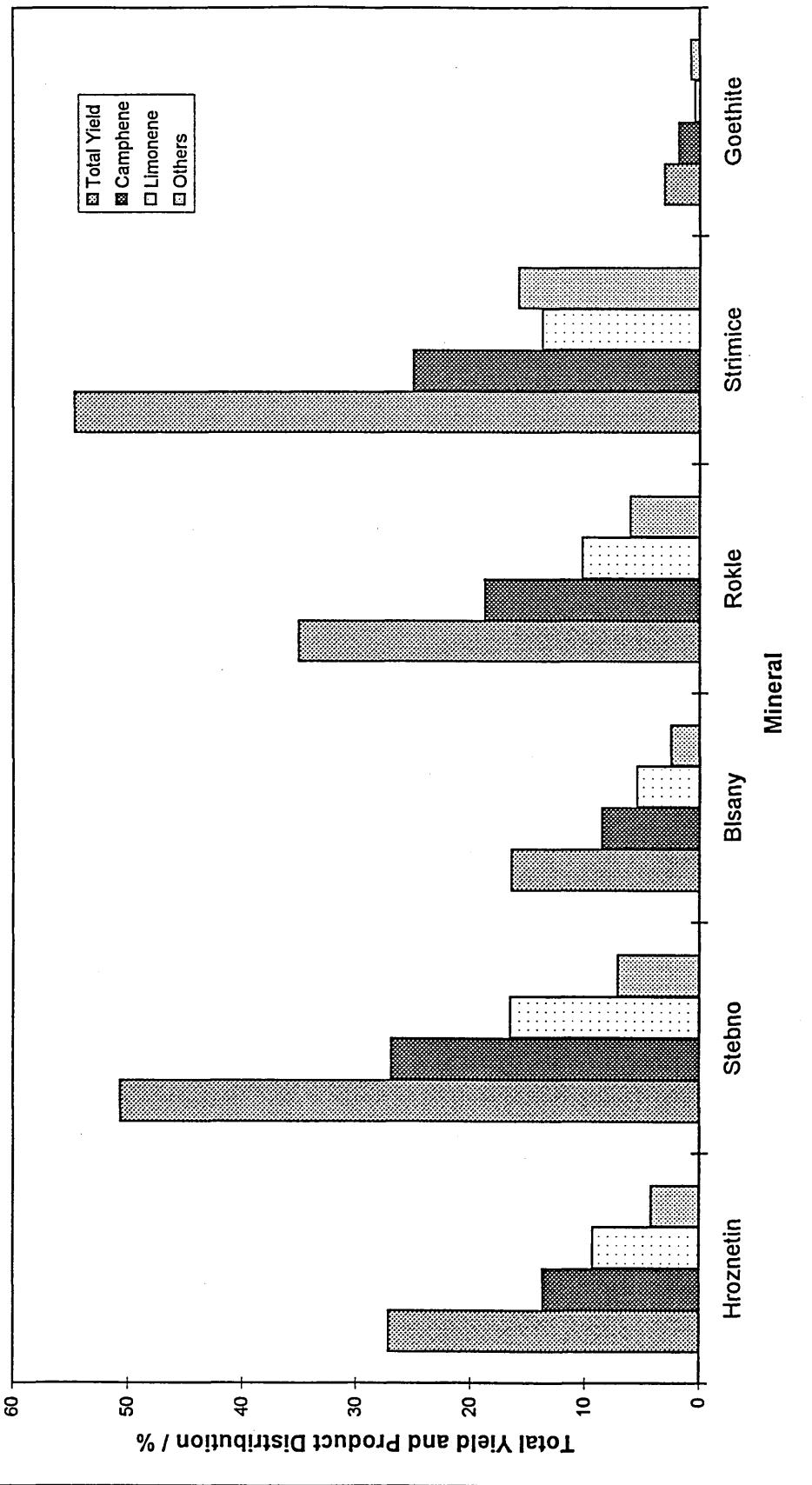


Figure 49. Showing the total yield and product distribution of minerals with varying iron content.

spacing was obtained indicating that the polycation, with its multiple exchange sites, was effectively binding the clay layers together.

Tricyclene was not identified in any of the product mixtures analysed herein, nor was it indicated by Rhodes and Brown²⁷⁰. Indeed, no oxidation products were identified in any of the product mixtures analysed herein, although the structural iron in ST and SWa-1 and SWy-2 present potential sites for redox reactions. Untreated ST is known to have a considerable amount of iron as goethite (α -FeOOH), (21% of total iron)²⁹⁷ and SWa-1 has a high iron content in its structure and about 3% of total iron is bound in goethite.

In order to investigate the effect of iron content further, a series of layer silicates containing a range of goethite contents were acquired and tested for catalytic activity, namely Hroznatin (8% iron in goethite, 6% structural), Blsany (37% iron in goethite), Rokle (50% iron in goethite) and Strimice (67% iron in goethite). The samples were neither exchanged with organic cations nor acid leached. Figure 49 shows that all smectites were catalytically active, however, there was no correlation between the goethite content and the percentage conversion of α -pinene. The very low yield from goethite suggested that the pure goethite species alone does not contribute substantially to the catalytic activity. However, it is well known that iron oxides and hydroxides in the fine fractions of bentonites are often of small crystal size, have a high defect concentration and a part of iron atoms are substituted by aluminium, therefore their properties differ from those of the pure iron oxides/hydroxides²⁹⁷. Microcrystallinity and/or Al^{3+} for Fe^{3+} substitution could affect the catalytic activity of the clays investigated. Also, the selectivity of Strimice (67% iron in goethite) and goethite is different to the other mineral species.

7.4 SUMMARY OF CATALYSIS INVESTIGATIONS.

It has been shown that, in general, catalysts exchanged with TMA⁺ cations show significantly enhanced activity compared to those catalysts containing DDTMA⁺ or ODTMA⁺ cations, for example JP-M3-4 (containing TMA⁺ cations) gave 80% total yield compared to JP-L3-4 (containing DDTMA⁺ cations), which gave 2% total yield and JP-O3-4 (containing ODTMA⁺ cations), which gave 3% total yield. The notable exceptions were ST-L1-2, ST-L1-60, ST-O1-2, ST-O1-60 and SWa-L1-60 which gave total yields of 80, 87, 70, 80 and 86% respectively. For the Slovak clays, the presence of organic cations enhances catalytic activity relative to those clays which have only been acid treated. This is also true for catalysts derived from SAz-1 which contain low loadings of polymer, for example SAz-32-90H produced 43% camphene whereas SAz-90 produced only 25% camphene. Conversely, for SWy-2 catalytic activity has not, in general, been enhanced by the presence of polycation relative to those clays which have only been acid treated, although acid treatment alone results in significant catalytic activity. The only exceptions are those catalysts containing a low loading of polymer which have been harshly acid treated, i.e. SWy-17-90H and SWy-17-180H. These samples show enhanced activity compared to the greatest conversion achieved by acid-activation of the base clays. That clays exchanged with the DDTMA⁺ or ODTMA⁺ cations were only effective when 30% of the exchange sites were occupied, is similar to the yields and selectivities found for polycation treated clays in that activity decreases markedly with loading.

The optimised TMA⁺ containing samples prepared using the competitive adsorption process have been shown to exhibit comparable activity to the samples prepared using the usual method. For example, SWy-2 competitively exchanged with 0.86 mmol

TMA⁺/48 mmol H⁺ (Figure 46 b), produced 42% camphene, compared with JP-M3-4 which produced 45% camphene.

Rhodes and Brown²⁷⁰ showed that the activity of acid-activated Texas bentonite for the isomerisation of α -pinene increased as the extent of acid leaching increased, reaching a maximum as the available surface area maximised and then diminished to zero. They convincingly argued that the clay surface became more like hydrophobic silica than hydrophilic aluminosilicate as the leaching progressed and thus the surface became more attractive to the non-polar α -pinene. In general, the data presented herein for the clays without adsorbed polycation conform to that interpretation. The total conversion of α -pinene by hot (harshly) acid-treated SAz-1 samples was more than three times that for room temperature (mildly) acid treated samples (Figure 45a), whilst treatment of SWy-2 at 95°C doubled the yield obtained from the samples treated at 25°C (Figure 45b). Nonetheless, the samples derived from SWy-2 were very effective catalysts for the α -pinene conversion even when the XRF (Table 19) data suggested that the clay maintained a considerable amount of lamellar character. MAS NMR studies of SAz-1²¹⁸ and SWy-1²⁹⁸ leached in hot 6M HCl support the view that SAz-1, which has a higher octahedral magnesium population than SWy-2, is leached more rapidly. Therefore, samples derived from SAz-1 were anticipated to attain the necessary hydrophobicity at shorter activation times. This was clearly not the case so the extent of acid activation cannot make the sole significant contribution to the activity for the isomerisation of α -pinene.

There is some evidence that the amount of octahedral iron plays a role in the activity insofar as mildly acid treated (0.1 M HCl at 25°C) JP, which is rich in octahedral

aluminium, shows very little activity over the untreated material. Moreover ST, an iron-rich beidellite with a high octahedral $\text{Fe}^{2+/\text{3}+}$ content, exhibited a high initial activity for α -pinene conversion and was very active (90% total conversion) after 60 minutes leaching in 6.0 M HCl at 25°C. Therefore, the amount of octahedral iron in the clay appears to influence the catalytic ability.

It is also thought that the activity of the catalyst also reflects its ability to swell in the organic solvent. SWy-2 contains a large proportion of Na^+ ions on its exchange sites and is known to swell more in aqueous solution than SAz-1 which is rich in Ca^{2+} exchange ions. The greater activity of catalysts derived from SWy-2 compared to catalysts derived from SAz-1 may reflect the greater surface area SWy-2 potentially offers in organic solvents.

Clearly, these initial results show that acid-activated organoclays have potential as a novel class of catalysts, however further work is required to optimise the type of organic cation and content required, in conjunction with acid treatment conditions for a wide range of catalytic reactions.

CHAPTER 8

Conclusions and Future Work.

8. INTRODUCTION.

The interaction of the polymer, Magnafloc 206, with a range of clays has been investigated. The behaviour of organoclays derived from high charge SAz-1 and low charge SWy-1 and SWy-2 have then been investigated for their potential as sorbents and as catalysts. They have been compared with TMA^+ exchanged counterparts which constitute organoclays of a contrasting nature. The 15 main findings will now be summarised in numerical order. These are subdivided by subject headings and appropriate additional information.

8.1 (POLY)CATION INTERACTIONS WITH CLAY MINERALS.

1. Polycations (Magnafloc 206), have a higher affinity than tetramethylammonium cations (TMA^+), for all clays studied.

It has been shown (Section 5.2.1, Figure 19), that the polymer, Magnafloc 206, has a higher affinity for the clays studied than TMA^+ cations. When simple inorganic cations, such as Na^+ , are added to a clay suspension, the quantity of exchangeable cation displaced is thought to depend largely on the hydration energy of the added cation. Like inorganic cations, TMA^+ , which has a cation hydration energy of -134 kJ/mol, adsorbs via ion exchange. In addition, van der Waals forces also play a role in the adsorption mechanism of this cation. Q_{\max} for TMA^+ adsorption on all clays investigated was lower than that for polymer adsorption. Q_{\max} for TMA^+ uptake by unsedimented, heterionic SAz-1 was 65 mg/g (72% CEC), as compared to Q_{\max} for polymer uptake by unsedimented, heterionic SAz-1 which was 160 mg/g (131% CEC). As the molecular size of alkylammonium cations increases, the affinity for the clay surface increases due to the increased contribution of van der Waals forces as the size of the cation is increased. The lower affinity of TMA^+ cations for the clay surface is shown by the less

steep initial rise in the uptake curves.

Polycations are adsorbed via cation exchange of an exchangeable cation associated with the clay for a cationic unit from the polymer. The high affinity of the polycations for the clay surface arises because the net segment-surface interaction energy, ϵ , is equal to approximately $4 kT$ per cationic unit. As there are many adsorbed segments per polymer molecule there is a large total energy of adsorption. In addition, alternate N groups on the polymer used in this thesis closely match the distance between negative sites on the clay surface. The polymers used in this work are very small in size when compared to the size of the clay particles. It is thought that when the polymer is adsorbed onto the surface of the clay there is not a uniform neutralisation of charge. This uneven distribution of charge leads to an extra attractive contribution to the interaction energy between two such particles. Flocculation occurs as a result of a positively charged, polymer rich patch of one particle coming into contact with a negatively charged, polymer free patch on another, known as the electrostatic patch model. Particle size and electrophoretic measurements in aqueous solution could be used to investigate this further.

2. The nature of the exchangeable cation and the degree of platelet dispersion

determines the amount of Magnafloc 206 adsorbed.

It has been shown (Section 5.2.1, Figure 24), that the nature of the exchangeable cation associated with the clay and therefore the degree of platelet dispersion plays a major role in determining the quantity of cationic species adsorbed. Deflocculated suspensions of Na-montmorillonite allow the polymer access to the total surface area of the clay. Conversely, the aggregation of platelets of Cs-montmorillonite results in reduced

accessibility of polymer to the clay surface and hence this clay shows reduced Q_{max} values.

Interlayer swelling and tactoid formation could be studied further by comparing the adsorption of polycations by clays exchanged with other ions, such as Li^+ , K^+ , Mg^{2+} , or Ca^{2+} to give different degrees of interlayer spacing and dispersion, with adsorption by other negatively charged particles such as silica which do not swell.

3. The ionic strength of the medium affects polymer uptake.

It was found (Section 5.2.1, Figure 25), that increasing the ionic strength of the medium increased Magnafloc 206 uptake at high initial nitrogen concentrations. Without added salt it is thought that the predominant type of platelet aggregation in heterionic clay suspensions is EF (edge-face). As the saline concentration increases it is thought that increased amounts of EE (edge-edge), bonded platelets are found thus leading to an increase in surface area of the clay and an increase in polymer uptake.

4. Polycations reside in the clay interlayer and there may be more than one layer present.

XRD data (Section 5.2.2, Figure 27), indicates that the polymer resides between the layers and in some interlayers of the clay there is more than one polymer layer present. Indeed the uptake curves show that polymer is often adsorbed in excess of the CEC. The basal spacing of polymer clay is thermally stable to 150°C at low loadings and to over 250°C at higher loadings. It has also been shown (Section 5.2.2, Figure 26), that TMA^+ cations are present within the interlayer, are more thermally stable than the polymer, and can prop the layers apart even when the system is dehydrated. The TG

analysis results (Section 5.2.3, Figure 28), confirmed the thermal stability of the organoclay complexes and support the interpretations of the adsorption isotherms.

The correlation between the data obtained is not surprising since the samples all underwent similar preparation procedures. A significant point however is that Kjeldahl, TG and XRD analyses were carried out on dried samples. This may not reflect the true situation in suspension before centrifugation and drying, or when dried samples are resuspended in water. When the samples are dried some counter ions must remain present to achieve charge neutrality, and it was found that the weight of Cl^- increases with increasing amounts of adsorbed polymer (Section 5.2.1, Figure 23). However, the precise mechanism by which these counter ions are incorporated has not yet been determined. Also, samples analysed by Kjeldahl and TG analysis underwent centrifugation procedures which may have affected the natural diffusion of polycationic species by allowing any previously unattached cationic groups to contact exchange sites on the clay particles. This may result in the dried samples exhibiting higher polycation uptake than is found in aqueous suspension during preparation. However, in using these techniques it was not possible to study the situation in suspension and they are not relevant to the work on pollutant adsorption or catalysis where the organoclays are prepared as dry powders. Further work could investigate the situation in suspension.

The adsorption of TMA^+ could be investigated further by studying the effect of its addition to Na-montmorillonite. It would be expected that one TMA^+ cation (hydration energy -134 kJ/mol), would replace one Na^+ cation (hydration energy of -405 kJ/mol), at the clay surface due to its much less negative hydration energy. Hence, a graph of the concentration of TMA^+ added versus the concentration of Na^+ detected would be a

straight line, thus confirming the hypothesis.

8.2 POLLUTANT ADSORPTION.

5. The uptake of benzene by TMA-SAz-1 and TMA-SWy-1 are as reported in the literature.

SAz-1 and SWy-1 exchanged with TMA⁺ and Magnafloc 206 have been investigated as sorbents for benzene and *p*-nitrophenol. The uptake of benzene by TMA-SAz-1 and TMA-SWy-1 was as reported in the literature (Section 6.1, Figure 30), and was used both as a benchmark for the sorption capabilities of the polycation exchanged sorbents and as confirmation of the efficacy of the experimental procedure.

6. The uptake of both benzene and *p*-nitrophenol by TMA-SAz-1 was significantly lower than by TMA-SWy-1.

It is thought that the predominant adsorption site on the TMA⁺ containing sorbents is the siloxane surface in the clay interlayers. This is supported by the observation that the uptake of both benzene and *p*-nitrophenol by TMA⁺ treated high charge SAz-1 was reduced compared to TMA⁺ treated low charge SWy-1 (Section 6.1, Figure 30 and Section 6.2, Figure 35). In SAz-1 there will be closer packing of adsorbed TMA⁺ cations resulting in less siloxane surface area being available. There are also steric constraints in that as the cation packing density increases, access to the clay surface becomes more hindered. This problem is exaggerated by the hydration of TMA⁺ in water which further reduces accessibility. Also, the uptake of benzene on TMA-SWy-1 was greater than the uptake of *p*-nitrophenol which is in agreement with the findings for shape selectivity reported in the literature.

Future work on surface adsorptive clays exchanged with TMA⁺ could extend previous studies by examining a range of clays with different charge densities with regard to their ability to adsorb a range of aromatic pollutants from water. Such results could be compared with TMA⁺ exchanged and polymer exchanged illites which would be informative since illites do not have the ability to swell.

7. High loadings of polymer reduce pollutant uptake.

As discussed previously (Section 5.2.1 and Point 1 above), it is thought that flocculation in the polymer exchanged system occurs via the electrostatic patch model. This results in face to face aggregation which will reduce the surface area available for adsorption of pollutants. This is in contrast to TMA⁺ treated clays which tend to form deflocculated aggregates. Therefore an increase in polymer loading may lead to increased aggregation which will further reduce the available surface area. The VT-XRD results presented herein (Section 5.2.2, Figure 27), show that at low loadings of polymer (e.g. 25 mg polymer/g clay), where the CEC is not satisfied, the polymer is segregated in different interlayers. It is thought that the clay has the ability to swell further on the addition of adsorbing species thus allowing adsorption of pollutants. Conversely, at higher polymer loadings adsorption onto the silicate surface is prevented and partition into the polymer organic phase occurs.

8. Adsorption of *p*-nitrophenol by partition does not increase with organic carbon content.

It has been shown (Section 6.2, Figure 32), that only low loadings of Magnafloc 206 (46 mg/g or less), are better at adsorbing *p*-nitrophenol than the untreated clay which supports the theory that the siloxane surface is the predominant adsorption site. Higher

loadings of Magnafloc 206 (> 46 mg/g), hinder the adsorption of the organic species by preventing access to the siloxane surface which may be a steric effect although the floc structure and particle size distribution of the treated clays may also be contributing. Also, high polymer loadings result in large areas of organic carbon (polymer chains), in the interlayer space which are inaccessible to *p*-nitrophenol and so partition only occurs in the outer regions. Hence, adsorption of *p*-nitrophenol does not increase with organic carbon content which is contrary to the usual findings when partition mechanisms are occurring.

9. Clay exchanged with a hydrophobic polymer adsorbs less *p*-nitrophenol.

Clay exchanged with the polymer PAA (poly(allylamine hydrochloride)), which is expected to be fully hydrophobic, was compared with clay exchanged with Magnafloc 206, which contains an -OH group, with respect to their ability to adsorb *p*-nitrophenol.

SWy-1 exchanged with the polymer PAA surprisingly showed a reduced ability to adsorb *p*-nitrophenol compared to clays exchanged with Magnafloc 206 (Section 6.2, Figure 34). The different nature of the monomer units is thought to affect the floc structure but further work is necessary to investigate this.

10. Adsorption of *p*-nitrophenol is related to Cs^+ content.

A relationship between Cs^+ content and uptake of *p*-nitrophenol has been observed (Section 6.2, Figure 36). As the amount of Cs^+ cations present in Cs-SWy-1 decreases due to displacement by polymer, so does the uptake of *p*-nitrophenol decrease which suggests that *p*-nitrophenol interacts with the Cs^+ cations rather than the siloxane surface. An in-situ study using ^{133}Cs solution phase NMR, such as that which has been

reported in the literature (discussed in Section 3.10.6.1), coupled with particle size and electrophoretic measurements in aqueous solution could be employed to investigate this further. Such investigations could also be used to assess how the sample preparation methods reported in this thesis affect the structure of the polymer treated clay.

11. WL does not behave like SWy-1 as expected from the CEC.

Based on the CEC alone, adsorbents derived from WL (Westone-L), should behave like adsorbents derived from SWy-1 for the uptake of benzene and *p*-nitrophenol, but it has been shown that this is not the case (Section 6.1, Figure 30). WL actually behaves more like SAz-1 in this respect therefore the CEC cannot be the only explanation. It is thought that exposure of the siloxane surface is important which will be affected by dispersion in solution. All of the modified clays used herein have been dried, then rehydrated in order to study adsorption from solution. How this affects the structure of the organoclays and their dispersion in solution is not fully understood, but is thought to be significant and should be investigated in future work. In-situ studies and particle size measurements, such as those mentioned in Point 10 above, could be part of such investigations.

It is thought that further development of this work, such as determining optimum (poly)cation loadings for adsorption of specific pollutants, may lead to organoclays being used as economically viable agents in applications such as the removal of particular pollutants from potable water supplies, and as landfill liners to prevent leaching of hazardous species.

8.3 CATALYSIS.

A range of organoclays containing TMA^+ , ODTMA^+ (octadecyltrimethylammonium), DDTMA^+ (dodecyltrimethylammonium) cations and polycations (MagnaFloc 206) at differing exchange levels have been subjected to acid leaching at either 25 or 90°C. The activity of these acid-activated (poly)cation-exchanged clays for the conversion of α -pinene to camphene and limonene was determined and compared with that from clay samples (without (poly)cations), acid treated in the same manner.

The clays investigated were JP (Jelsovy Potok), a montmorillonite rich in octahedral aluminium; SWa-1 a ferruginous smectite; ST (Stebno) an iron rich beidellite with a high octahedral Fe^{3+} content; SAz-1, a magnesium rich montmorillonite; and SWy-2 an aluminium rich montmorillonite.

12. Acid-activated TMA^+ exchanged clays are generally the most active.

Acid treatment of tetraalkylammonium-exchanged clays produced hybrid catalysts which enhanced the activity of the clays for the isomerisation of α -pinene to camphene by a factor of four (Section 7.3). This enhancement in yield is attributed to the increased hydrophobicity of the organoclay. Acid-activated TMA^+ exchanged clays are, in general, the most active of those catalysts studied.

13. Catalysts containing small amounts of polycation show significant activity.

Harsh acid treatment of low loading polycation exchanged catalysts produce comparable activity to the most active TMA^+ containing catalysts, which is 60-90% conversion based on α -pinene (Section 7.3, Figure 45). These yields are directly comparable with those

obtained using zeolites and pillared clays as reported in the literature, although the acid-activated organoclays used herein are marginally less selective towards camphene.

The presence of small amounts of polycation had a marked influence on the activity of samples derived from SAz-1 increasing the yield from 25% for acid-activated SAz-1 with no added polycation, to 50% camphene for acid-activated polycation-exchanged SAz-1. The increase in yield for corresponding samples derived from SWy-2 was only from 42 to 52%. This enhancement in yield for samples derived from SAz-1 was again attributed to the increased hydrophobicity of the polycation loaded clay, whilst the comparable yields for SWy-2 in the absence and presence of polycation may suggest that SWy-2 disperses well in the non-polar α -pinene.

14. Octahedral iron content affects catalytic activity.

It has been shown (Section 7.3, Figure 41), that the octahedral iron content appears to affect activity since the iron containing smectites ST and SWa-1 were more active than JP which is rich in octahedral aluminium .

15. Catalysts prepared by the competitive adsorption approach show comparable activity to the usual high temperature methods of preparation.

Catalysts derived from SAz-1 and SWy-2 that were prepared by the competitive adsorption of TMA^+ and H^+ at room temperature showed comparable activity to those catalysts that were first exchanged with TMA^+ and then harshly acid-activated (Section 7.3, Figure 43). This suggests that such a competitive adsorption approach could be used in future to produce lower cost catalysts and also avoid the increased hazard of using mineral acids at elevated temperatures.

The acid-activated organoclays show great potential as inexpensive, easily prepared catalysts but further work to optimise conditions for a wide range of reactions will be required to fully explore their capabilities.

CHAPTER 9

Postgraduate Study, Articles in Preparation and References.

9.1 POSTGRADUATE STUDY.

Courses and Conferences attended during this period of research are listed below:

Date	Location	Course / Conference	Duration
1993-1996	Sheffield Hallam University	School of Science Seminars	Weekly
1994	Sheffield Hallam University	Vibrational Spectroscopy Course	8 x 2 hours
1995	Sheffield Hallam University	X-Ray Techniques	16 x 1 hour
14-15 September 1995	Lancaster University	Minerological Society, Clay Minerals Group 1996 Autumn Conference*	2 days
1-2 April 1996	Sheffield Hallam University	Minerological Society, Clay Minerals Group 1996 Spring Conference**	2 days

* A presentation entitled 'The Influence of Mineral Type, Sample Purification and Salinity of the Exchange Medium on the Adsorption of Polyammonium Cation on Clays' by R. Watson and C. Breen was given at this Conference

**A poster entitled 'The Influence of Mineral Type, Sample Purification and Salinity of the Exchange Medium on the Adsorption of Polyammonium Cation on Clays' was presented at this Conference.

9.2 ARTICLES IN PREPARATION.

The following articles have been submitted for publication:

Acid-Activated Organoclays: Preparation, Characterisation and Catalytic Activity of Acid Treated Tetra-Alkylammonium Exchanged Smectites.
C. Breen, R. Watson, J. Madejová, P. Komadel, Z. Klaptya. (Submitted to Langmuir.)

Acid-Activated Organoclays: Preparation, Characterisation and Catalytic Activity of Polycation-Treated Bentonite.
C. Breen, R. Watson. (Submitted to Applied Clay Science.)

The following articles are in preparation:

Polycation-Exchanged Clays as Sorbents for Organic Pollutants.
R. Watson, C. Breen. (For submission to Clay Minerals.)

Acid-Activated Organoclays: Preparation, Characterisation and Catalytic Activity of Tetramethylammonium Exchanged Clays of Varying Octahedral Magnesium Content.
C. Breen, R. Watson, A. Moronta.

9.3 REFERENCES.

- ¹ Council on Environmental Quality, Contamination of Groundwater by Toxic Organic Chemicals, U.S. Government Printing Office, Washington, D.C., 1981.
- ² United States Environmental Protection Agency, Groundwater Protection Strategy, Office of Groundwater Protection, Washington, D.C., 1984.
- ³ United States Environmental Protection Agency, Pesticides in Groundwater Database. A Compilation of Monitoring Studies, 1971-1991, National Summary, Washington, D.C., 1992.
- ⁴ C. Rav-Acha, M Rebhun, Binding of Organic Solutes to Dissolved Humic Substances and its Effects on Adsorption and Transport in the Aquatic Environment, *Wat. Res.*, **26**, 12, 1645-1654, 1992.
- ⁵ T. Undebeytia, E. Morillo, C. Maqueda, Simultaneous Adsorption of Cadmium and a Cationic Pesticide on Montmorillonite, *Toxicol. and Environ. Chem.*, **43**, 77-84, 1994.
- ⁶ C. D. Brown, R. A. Hodgkinson, D. A. Rose, J. K. Syers, S. J. Wilcockson, Movement of Pesticides to Surface Waters from a Heavy Clay Soil, *Pestic. Sci.*, **43**, 131-140, 1995.
- ⁷ B. L. Sawhney, R. P. Kozloski, Organic Pollutants in Leachates from Landfill Sites, *J. Environ. Qual.*, **13**, 349-352, 1984.
- ⁸ J. W. Jordan, Organophilic Bentonites, I. Swelling in Organic Liquids. *J. Phys. Colloid. Chem.*, **53**, 294-306, 1949.
- ⁹ R. M. Barrer, D. M. MacLeod, Activation of Montmorillonite by Ion Exchange and Sorption Complexes of Tetra-Alkyl Ammonium Montmorillonites, *Trans. Faraday Soc.*, **51**, 1290-1300, 1955.
- ¹⁰ R. M. Barrer, Shape-Selective Sorbents Based on Clay Minerals, *Clays and Clay Miner.*, **37**, 5, 385-395, 1989.
- ¹¹ J. F. Lee, J. R. Crum, S. A. Boyd, Enhanced Retention of Organic Contaminants by Soils Exchanged with Organic Cations, *Environ. Sci. Tech.*, **23**, 1365-1372, 1989.
- ¹² A. Guyot, R. Audebert, R. Botet, B. Cabane, F. Lafuma, R. Julien, E. Pefferkorn, C. Pichot, A. Revillon, R. Varoqui, Flocculation de Particules Colloidales par les Polymères Hydrosolubles, *J. Chim. Phys.*, **87**, 1859-1899, 1990.
- ¹³ L. H. Keith, W. A. Telliard, Priority Pollutants, I - A Perspective View, *Environ. Sci. Tech.*, **13**, 4, 416-423, 1979.
- ¹⁴ D. R. Burris, C. P. Antworth, In-site Modification of an Aquifer Material by a Cationic Surfactant to Enhance Retardation of Organic Contaminants, *J. Contaminant Hydrology*, **10**, 325-337, 1992.

-
- ¹⁵ M. Harper, C. J. Purnell, Alkylammonium Montmorillonites as Adsorbents for Organic Vapours from Air, *Environ. Sci. Technol.*, **24**, 1, 55-62, 1990.
- ¹⁶ I. V. Mitchell, Pillared Layered Silicates, Elsevier Applied Science, London, 252, 1990.
- ¹⁷ S. A. Boyd, M. M. Mortland, Selective Effects of Smectite-Organic Complexes on the Activities of Immobilized Enzymes, *J. Molec. Catal.*, **34**, 1-8, 1986.
- ¹⁸ M. K. H. Siddiqui, Bleaching Earths, Pergamon Press, Oxford, 86, 1968.
- ¹⁹ D. A. Morgan, D. B. Shaw, M. J. Sidebottom, T. C. Soon, R. S. Taylor, The Function of Bleaching Earths in the Processing of Palm, Palm Kernel and Coconut Oil, *J. Am. Oil Chem.*, **62**, 292-299, 1985.
- ²⁰ R. Mokaya, W. Jones, M. E. Davies, M. E. Whittle, The Mechanism of Chlorophyll Adsorption on Acid Treated Clays, *J. Solid State Chem.*, **111**, 157-163, 1994.
- ²¹ R. Fahn, K. Fenderl, Reaction Products of Organic Dye Molecules with Acid Treated Montmorillonite, *Clay Miner.*, **18**, 447-458, 1983.
- ²² J. M. Adams, Synthetic Organic Chemistry Using Pillared, Cation-Exchanged and Acid Treated Montmorillonite Catalysts - A Review, *Appl. Clay Sci.*, **2**, 309-342, 1987.
- ²³ C. Breen, Thermogravimetric Study of the Desorption of Cyclohexylamine and Pyridine from an Acid Treated Wyoming Bentonite, *Clay Miner.*, **26**, 473-486, 1991.
- ²⁴ C. Breen, Thermogravimetric Study and Infrared Study of the Desorption of Butylamine, Cyclohexylamine and Pyridine from Ni- and Co- Exchanged Montmorillonite, *Clay Miner.*, **26**, 487-496, 1991.
- ²⁵ C. N. Rhodes, M. Franks, G. M. B. Parkes, D. R. Brown, The Effect of Acid Treatment on the Activity of Clay Supports for $ZnCl_2$ Alkylation Catalysts, *J. Chem. Soc. Chem. Commun.*, 805-807, 1991.
- ²⁶ V. Krishnasamy, V. Mohan, Utilization of Indian Turpentine. Catalytic Transformation Studies of α -Pinene, 3-Carene, Camphene and Tricyclene to Cymenes: Kinetic Aspects, *J. Indian Chem. Soc.*, Vol. LX, 359-363, 1983.
- ²⁷ D. Winter, G. Zubay, Binding of Adenine and Adenine-Related Compounds to the Clay Montmorillonite and the Mineral Hydroxylapatite, *Origins of Life and Evolution of the Biosphere*, **25**, 61-81, 1995.

-
- ²⁸ M. A. Vicente, M. Sánchez-Camazano, M. J. Sánchez-Martin, M. Delario, C. Martin, V. Rives, J. Vicente-Hernandez, Adsorption and Desorption of N-Methyl 8-hydroxyl Quinoline Methyl Sulphate on Smectite and the Potential Use of the Clay-Organic Product as an Ultra-Violet Radiation Collector, *Clays and Clay Miner.*, **37**, 157-163, 1989.
- ²⁹ S. Guggenheim, R. T. Martin, Definition of Clay and Clay Minerals: Joint Report of ther AIPEA Nomenclature and CMS Nomenclature Committees, *Clays and Clay Miner.*, **43**, 2, 255-256, 1995
- ³⁰ R. E. Grim, Clay Mineralogy, 2nd Edition, McGraw Hill, London, 1968.
- ³¹ A. A. Damour, D. Salvetat, Et Analyses sur un Hydrosilicate D'alumine Trouve a Montmorillon, *Ann. Chim. Phys.*, ser 3, **21**, 376-383, 1847.
- ³² U. Hofmann, K. Endell, D. Wilm, Kristallstruktur und Quellung von Montmorillonite, *Z. Krist.*, **86**, 340-348, 1933.
- ³³ C. E. Marshall, Layer Lattices and Base Exchange Clays, *Z. Krist.*, **91**, 433-449, 1935.
- ³⁴ E. Maegdefrau, U. Hofmann, Die Kristallstruktur des Montmorillonite, *Z. Krist.*, **98**, 299-323, 1937.
- ³⁵ S. B. Hendricks, Lattice Structure of Clay Minerals and Some Properties of Clays, *J. Geol.*, **50**, 276-290, 1942.
- ³⁶ C. H. Edelman, J. C. L. Favejee, On the Crystal Structure of Montmorillonite and Halloysite, *Z. Krist.*, **A102**, 417-431, 1940.
- ³⁷ D. McConnell, The Crystal Chemistry of Montmorillonite, *Am. Mineralogist*, **35**, 166-172, 1950.
- ³⁸ H. van Olphen, An Introduction to Clay Colloid Chemistry, Interscience, New York, 1977.
- ³⁹ C. N. Rhodes, D. R. Brown, Rapid Determination of the Cation Exchange Capacity of Clays using Co(II), *Clay Miner.*, **29**, 799-801, 1994.
- ⁴⁰ G. Burrafato, F. Miano, Determination of the Cation Exchange Capacity of Clays by Surface Tension Measurements, *Clay Miner.*, **28**, 475-481, 1993.
- ⁴¹ C. Bardon, Recommandations pour la Détermination Expérimentale de la Capacité d'Échange de Cations Milieux argileux, *Revue de l'Institute Français du Petrole*, **38**, 5, Sept.-Oct., 621-626, 1983.
- ⁴² G. Rytwo, C. Serban, S. Nir, L. Margulies, Use of Methylene Blue and Crystal Violet for Determination of Exchangeable Cations in Montmorillonite, *Clays and Clay Miner.*, **39**, 5, 551-555, 1991.

-
- ⁴³ S. Hillier, T. Clayton, Cation Exchange 'Staining' of Clay Minerals in Thin Section for Electron Microscopy, *Clay Miner.*, **27**, 379-384, 1992.
- ⁴⁴ W. H. Hendershot, M. Duquette, A Simple Barium Chloride Method for Determining Cation Exchange Capacity and Exchangeable Cations, *Soil Sci. Soc. Am. J.*, **50**, 605-608, 1986.
- ⁴⁵ R.C. MacKenzie, A Micro-Method for Determining the Cation Exchange Capacity of a Clay, *J. Coll. Sci.* **6**, 219-222, 1951.
- ⁴⁶ R. W. Grimshaw, The Chemistry and Physics of Clays, (R. Benn, Ed.), London, 1971.
- ⁴⁷ P. B. Malla, M. Robert, L. A. Douglas, D. Tessier, S. Komarneni, Charge Heterogeneity and Nanostructure of 2:1 Layer Silicates by High-Resolution Transmission Electron Microscopy, *Clays and Clay Miner.*, **41**, 4, 412-422, 1993.
- ⁴⁸ C. Krishnamoorthy, R. Overstreet, An Experimental Evaluation of Ion Exchange Relationships, *Soil Sci.*, **69**, 41-53, 1950.
- ⁴⁹ L. Wilkander, Fixation of Potassium By Clays Saturated With Different Cations, *Soil Sci.*, **69**, 261-268, 1950.
- ⁵⁰ C. E. Marshall, G. Garcia, Exchange Equilibria in a Carboxylic Resin and in Attapulgite Clay, *J. Phys. Chem.*, **63**, 1663-1666, 1959.
- ⁵¹ J. B. Page, L. D. Beaver, Ionic Size in Relation to Fixation of Cations by Colloidal Clay, *Soil Sci. Soc. Am. Proc.*, **4**, 150-155, 1940.
- ⁵² J. I. Wear, J. L. White, Potassium Fixation in Clay Minerals as Related to Crystal Structure, *Soil Sci.*, **71**, 1-14, 1951.
- ⁵³ I. Shainberg, W. D. Kemper, Hydration Status of Adsorbed Cations, *Soil Sci. Soc. Am. Proc.*, **30**, 707-713, 1966.
- ⁵⁴ B. L. Sawhney, Selective Sorption and Fixation of Cations by Clay Minerals: A Review, *Clays and Clay Miner.*, **20**, 93-100, 1972.
- ⁵⁵ U. Hofman, R. Klemen, Verlust der Austauschfähigkeit von Lithiumionen an Bentonit durch Ehfitzung: *Anorg. Allg. Chem.*, **262**, 95-99, 1950.
- ⁵⁶ R. M. Barrer, Zeolites and Clay Minerals as Sorbents and Molecular Sieves, Chapter 8, Academic Press, 1978.
- ⁵⁷ K. Norrish, The Swelling of Montmorillonite, *Disc. Faraday Soc.*, **18**, 120-134, 1954.

-
- ⁵⁸ J. M. Cases, I. Bérend, G. Besson, M. François, J. P. Uriot, F. Thomas, J. E. Poirier, Mechanism of Adsorption and Desorption of Water Vapour by Homionic Montmorillonite. 1. The Sodium-Exchanged Form, *Langmuir*, **8**, 2730-2739, 1992.
- ⁵⁹ D. M. Clementz, T. J. Pinnavaia, M. M. Mortland, Stereochemistry of Hydrated Copper (II) Ions on the Interlamellar Surfaces of Layer Silicates. An Electron Spin Resonance Study, *J. Phys. Chem.*, **77**, 196-200, 1973.
- ⁶⁰ R. Prost, Interactions Between Adsorbed Water Molecules and the Structure of Clay Minerals: Hydration Mechanism of Smectites: *Proc. Int. Clay Conf.*, Clay Minerals Society, Mexico City, 351-359, 1975.
- ⁶¹ G. Sposito, R. Prost, Structure of Water Adsorbed on Smectites, *Chem. Rev.*, **82**, 553-573, 1982.
- ⁶² C. T. Johnstone, G. Sposito, C. Erickson, Vibrational Probe Studies of Water Interactions with Montmorillonite, *Clays and Clay Miner.*, **40**, 6, 722-730, 1992.
- ⁶³ Z. Zhou, Construction and Application of Clay-Swelling Diagrams by Use of XRD Methods, *J. Petrol. Tech.*, **47**, 306, 1995.
- ⁶⁴ Y. Tardy, J. Duplay, A Method of Estimating the Gibbs Free Energies of Formation of Hydrated and Dehydrated Clay Minerals, *Geochimica et Cosmochimica Acta*, **56**, 3007-3029, 1992.
- ⁶⁵ I. Bérend, J. M. Cases, M. François, J. P. Uriot, L. Michot, A. Masion, F. Thomas, Mechanism of Adsorption and Desorption of Water Vapour by Homionic Montmorillonites. 2. The Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺-Exchanged Forms, *Clays and Clay Miner.*, **43**, 3, 324-336, 1995.
- ⁶⁶ D. A. Laird, C. Shang, M. L. Thompson, Hysteresis in Crystalline Swelling of Smectites, *J. Coll. Inter. Sci.*, **171**, 240-245, 1995.
- ⁶⁷ P. G. Slade, J. P. Quirk, K. Norrish, Crystalline Swelling of Smectite Samples in Concentrated NaCl Solutions in Relation to Layer Charge, *Clays and Clay Miner.*, **39**, 3, 234-238, 1991.
- ⁶⁸ W. J. Moore, Physical Chemistry, 4th Edition, Longmans, 751-752, 1966.
- ⁶⁹ R. H. Bennett, M. H. Hulbert, *Clay Microstructure*: D. Reidel, Dordrecht, the Netherlands, 57-58, 1986.
- ⁷⁰ J. Stawinski, J. Wierzchos, M. T. Garcia-Gonzalez, Influence of Calcium and Sodium Concentration on the Microstructure of Bentonite and Kaolin, *Clays and Clay Miner.*, **38**, 6, 617-622, 1990.

-
- ⁷¹ H. van Olphen, Forces Between Suspended Bentonite Particles: in *Clays and Clay Miner., Proc. 4th Natl. Conf., University Park, Pennsylvania, 1955*, (A. Swineford, Ed.), Natl. Reg. Counc. Publ., 456, 204-223, 1956.
- ⁷² A. S. Michaels, J. Bolger, The Plastic Flow Behaviour of Flocculated Kaolin Suspension, *Ind. Eng. Chem. Fundam.*, 1, 153-163, 1963.
- ⁷³ W. T. Granquist, Flow Properties of Dilute Montmorillonite Dispersion: in *Clays and Clay Miner., Proc. 6th Natl. Conf., Berkeley, California, 1957*, (A. Swineford, Ed.), Pergamon Press, New York, 207-219, 1959.
- ⁷⁴ H. van Olphen, Internal Mutual Flocculation in Clay Suspension, *J. Coll. Inter. Sci.* 19, 313-322, 1964.
- ⁷⁵ R. Keren, D.L. Sparks, The Role of Edge Surfaces in Flocculation of 2:1 Clay Minerals, *Soil Sci. Soc. Am. J.*, 59, 430-435, 1995.
- ⁷⁶ L. L. Schramm, J. C. T. Kwak, Influence of Exchangeable Cation Composition on the Size and Shape of Montmorillonite Particles in Dilute Suspensions, *Clays and Clay Miner.*, 30, 1, 40-48, 1982.
- ⁷⁷ S. L. Swartzen-Allen, E. Matijevic, Colloid and Surface Properties of Clay Suspensions, *J. Coll. Inter. Sci.* 50, 1, 143-152, 1975.
- ⁷⁸ S. Yariv, L. Heller, Sorption of Cyclohexylamine by Montmorillonite, *Israel J. Chem.*, 8, 935-945, 1970.
- ⁷⁹ S. Yariv, The Effect Tetrahedral Substitution of Si by Al on the Surface Acidity of the Oxygen Plane of Clay Minerals, *Int. Rev. Phys. Chem.*, 11, 2, 345-375, 1992.
- ⁸⁰ B. K. G. Theng, The Chemistry of Clay-Organic Reactions, (A. Hilger, Ed.), London, 261-269, 1974.
- ⁸¹ U. Hofmann, K. Endell, D. Wilm, Röntgenographische un Kolloidchemische Untersuchungen Über Ton, *Angew. Chem.*, 47, 539-547, 1934.
- ⁸² C. R. Smith, Base Exchange Reactions of Bentonites and Salts of Organic Bases, *J. Amer. Chem. Soc.*, 56, 1561-1563, 1936.
- ⁸³ J. F. Lee, M. M. Mortland, S. A. Boyd, C. T. Chiou, Shape-Selective Adsorption of Aromatic Molecules from Water by Tetramethylammonium-Smectite, *J. Chem. Soc., Faraday Trans. I*, 85, 9, 2953-2962, 1989.
- ⁸⁴ W. F. Jaynes, S. A. Boyd, Trimethylphenylammonium-Smectite as an Effective Adsorbent of Water Soluble Aromatic Hydrocarbons, *J. Air Waste Manage. Assoc.*, 40, 1649-1653, 1990.
- ⁸⁵ J. P. Bromberg, Physical Chemistry, Allyn and Bacon, Boston, 882-886, 1980.

-
- ⁸⁶ S. W. Karichoff, D. S. Brown, T. A. Scott, Sorption of Pollutants on Natural Sediments, *Water Research*, **13**, 241-250, 1979.
- ⁸⁷ R. D. Schwarzenbach, J. Westall, Transport of Non-Polar Organic Compounds From Surface Water to Ground Water - Laboratory Sorption Studies, *Environ. Sci. Technol.*, **15**, 1360-1367, 1981.
- ⁸⁸ W. J. Weber Jr., T. C. Voice, M. Pirbazari, G. Hunt, D. M. Ulanoff, Sorption of Hydrophobic Compounds by Sediments, Soils and Suspended Solids. 2. Sorbent Evaluation Studies, *Water Research*, **17**, 1443-1453, 1983.
- ⁸⁹ D. J. Greenland, R. H. Laby, J. P. Quirk, Adsorption of Glycine and its Di-, Tri-, and Tetra-Peptides by Montmorillonite, *Trans. Faraday Soc.*, **58**, 829-841, 1962.
- ⁹⁰ D. J. Greenland, R. H. Laby, J. P. Quirk, Adsorption of Amino Acids and Peptides by Montmorillonite and Illite, Part 2, *Trans. Faraday Soc.*, **61**, 2024-2035, 1965.
- ⁹¹ B. K. G. Theng, Adsorption of Ammonium and Some Primary n-Alkylammonium Cations by Soil Allophane, *Nature*, **238**, 150-151, 1972.
- ⁹² B. K. G. Theng, H. W. Scharpenseel, The Adsorption of ¹⁴C-labelled Humic Acid by Montmorillonite, in *Proc. Inter. Clay Conf., Mexico City*, (S. W. Bailey, Ed.), Applied Publishing, Wilmette, Illinois, 643-653, 1976.
- ⁹³ C. T. Chiou, L. J. Peters, V. H. Frees, A Physical Concept of Soil-Water Equilibria for Nonionic Organic Compounds, *Science*, **206**, 831-832, 1979.
- ⁹⁴ C. T. Chiou, P. E. Porter, D. W. Schmedding, Partition Equilibria of Nonionic Organic Compounds Between Soil Organic Matter and Water, *Environ. Sci. Technol.*, **17**, 227-231, 1983.
- ⁹⁵ J. A. Smith, P. R. Jaffe, C. T. Chiou, Effect of Ten Quaternary Ammonium Cations on Tetrachloromethane Sorption to Clay from Water, *Environ. Sci. Tech.*, **24**, 1167-1172, 1990.
- ⁹⁶ W. F. Jaynes, S. A. Boyd, Clay Mineral Type and Organic Compound Sorption by Hexadecyltrimethylammonium-Exchanged Clays, *Soil Sci. Soc. Am. J.*, **55**, 43-48, 1991.
- ⁹⁷ C. H. Giles, T. H. MacEwan, S. N. Nakhwa, D. Smith, Studies in Adsorption. XI. A System of Classification of Solution Adsorption Isotherms and its Use in Diagnosis of Adsorption Mechanisms and in Measurement of Specific Surface Areas of Solids, *J. Chem. Soc.* 3973-3993, 1960.
- ⁹⁸ D. M. C. MacEwan, Complexes of Clays with Organic Compounds, I. Complex Formation Between Montmorillonite and Halloysite and Certain Organic Liquids, *Trans. Faraday Soc.*, **44**, 349-367, 1948.

-
- ⁹⁹ R. C. MacKenzie, Complexes of Clays with Organic Compounds, II. Investigation of the Ethylene Glycol-Water-Montmorillonite System Using Karl Fischer Reagent, *Trans. Faraday Soc.*, **44**, 368-375, 1948.
- ¹⁰⁰ W. F. Bradley, Molecular Associations Between Montmorillonite and Some Polyfunctional Organic Liquids, *J. Amer. Chem. Soc.*, **67**, 975-981, 1945.
- ¹⁰¹ D. M. C. MacEwan, The Montmorillonite Minerals (Montmorillonoids), X-Ray Identification and Crystal Structures of Clay Minerals, Mineralogical Society, London, 86-137, 1951.
- ¹⁰² R. Greene-Kelly, Sorption of Aromatic Organic Compounds by Montmorillonite. Part 1 - Orientation Studies, *Trans. Faraday Soc.*, **51**, 412-424, 1955.
- ¹⁰³ R. Greene-Kelly, Sorption of Aromatic Organic Compounds by Montmorillonite. Part 2 - Packaging Studies with Pyridine, *Trans. Faraday Soc.*, **51**, 425-430, 1955.
- ¹⁰⁴ R. M. Barrer, J. S. S. Reay, Sorption and Intercalation by Methyl-Ammonium Montmorillonites, *Trans. Faraday Soc.*, **53**, 1253-1261, 1957.
- ¹⁰⁵ R. M. Barrer, G. S. Perry, Sorption of Mixtures and Selectivity in Alkyl-Ammonium Montmorillonites. Part I. Monomethylammonium Bentonite., *J. Chem. Soc.* 842-849, 1961.
- ¹⁰⁶ R. M. Barrer, G. S. Perry, Sorption of Mixtures and Selectivity in Alkyl-Ammonium Montmorillonites. Part II. Tetramethylammonium Montmorillonite., *J. Chem. Soc.*, 850-858, 1961.
- ¹⁰⁷ R. M. Barrer, K. Brummer, Relations Between Partial Ion Exchange and Interlamellar Sorption in Alkyl-Ammonium Montmorillonites. *Trans. Faraday Soc.*, **59**, 959-968, 1963.
- ¹⁰⁸ C. T. Cowan, D. White, Adsorption by Organoclay Complexes, *Clays and Clay Miner.*, **11**, 459-467, 1962.
- ¹⁰⁹ C. T. Cowan, Adsorption by Organoclay Complexes - Part 2 , *Clays and Clay Miner.*, **12**, 226-234, 1963.
- ¹¹⁰ W. H. Slabaugh, L. S. Carter, The Hydrophilic-Hydrophobic Character of Organomontmorillonites, *J. Coll. Int. Sci.*, **27**, 235-238, 1968.
- ¹¹¹ M. S. Stul, A. Maes, J. B. Uytterhoeven, The Adsorption of n-Aliphatic Alcohols from Dilute Aqueous Solutions on RNH Montmorillonites. Part II, Interlamellar Associations of the Adsorbate, *Clays and Clay Miner.*, **27**, 377-386, 1979.
- ¹¹² A. Weiss, Mica-Type Layer Silicates with Alkyl-Ammonium Ions; in *Clays and Clay Miner.*, *Proc. 10th Natl. Conf., Austin, Texas, 1961*, (A. Swineford, Ed.), Pergamon Press, New York, 191-224, 1963.

-
- ¹¹³ T. A. Wolfe, T. Demirel, E. R. Baumann, Interaction of Aliphatic Amines with Montmorillonite to Enhance Adsorption of Organic Pollutants, *Clays and Clay Miner.*, **33**, 301-311, 1985.
- ¹¹⁴ T. A. Wolfe, T. Demirel, E. R. Baumann, Adsorption of Organic Pollutants on Montmorillonite Treated with Amines, *Journal W.P.C.F.*, **58**, 1, 68-76, 1986.
- ¹¹⁵ R. B. Evans, G.E. Schweitzer, Assessing Hazardous Waste Problems, *Environ. Sci. Tech.*, **18**, 330-390, 1984.
- ¹¹⁶ M. B. McBride, T. J. Pinnavaia, M. M. Mortland, Adsorption of Aromatic Molecules by Clays in Aqueous Suspensions, *Adv. Env. Sci.*, **8**, 145-154, 1977.
- ¹¹⁷ M. M. Mortland, S. Shaobai, S. A. Boyd, Clay-Organic Complexes as Adsorbents for Phenol and Chlorophenols, *Clays and Clay Miner.*, **34**, 5, 581-585, 1986.
- ¹¹⁸ R. K. Kukkadapu, S. A. Boyd, Tetramethylphosphonium- and Tetramethylammonium-Smectites as Adsorbents of Aromatic and Chlorinated Hydrocarbons: Effect of Water on Adsorption Efficiency, *Clays and Clay Miner.*, **43**, 3, 318-323, 1995.
- ¹¹⁹ J. F. Lee, M. M. Mortland, C. T. Chiou, D. E. Kile, S. A. Boyd, Adsorption of Benzene, Toluene and Xylene by Two Tetramethylammonium-Smectites Having Different Charge Densities, *Clays and Clay Miner.*, **38**, 2, 113-120, 1990.
- ¹²⁰ W. F. Jaynes, S. A. Boyd, Hydrophobicity of Siloxane Surfaces in Smectites as Revealed by Aromatic Hydrocarbon Adsorption from Water, *Clays and Clay Miner.*, **39**, 4, 428-436, 1991.
- ¹²¹ F. A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, New York, Wiley Press, 507, 1966.
- ¹²² C. T. Chiou, P. E. Porter, T. D. Shoup, Partition Equilibria of Nonionic Organic Compounds Between Soil Organic Matter and Water, *Environ. Sci. Technol.*, **18**, 295-297, 1984.
- ¹²³ J. M. Brixie, S. A. Boyd, Organic Chemicals in the Environment, *J. Environ Qual.*, **23**, 1283-1290, 1994.
- ¹²⁴ S. A. Boyd, M. M. Mortland, C. T. Chiou, Sorption Characteristics of Organic Compounds on Hexadecyltrimethylammonium-Smectite, *Soil Sci. Soc. Am. J.*, **52**, 652-657, 1988.
- ¹²⁵ S. A. Boyd, S. Shaobai, J. F. Lee, M. M. Mortland, Pentachlorophenol Sorption By Organoclays, *Clays and Clay Miner.*, **36**, 2, 125-130, 1988.
- ¹²⁶ S. Xu, S. A. Boyd, Cationic Surfactant Adsorption by Swelling and Nonswelling Layer Silicates, *Langmuir*, **11**, 2508-2514, 1995.

-
- ¹²⁷ S. Xu, S. A. Boyd, Cationic Surfactant Sorption to a Vermiculitic Subsoil via Hydrophobic Bonding, *Environ. Sci. Tech.*, **29**, 29, 312-320, 1995.
- ¹²⁸ C. T. Chiou, T. D. Shoup, Soil Sorption of Organic Vapors and Effects of Humidity on Sorptive Mechanisms and Capacity, *Environ. Sci. Technol.*, **19**, 1196-1200, 1985.
- ¹²⁹ S. A. Boyd, J. F. Lee, M. M. Mortland, Attenuating Organic Contaminant Mobility by Soil Modification, *Nature*, **333**, 345-347, 1988.
- ¹³⁰ A. Patzko, I. Dekany, Ion Exchange and Molecular Adsorption of a Cationic Surfactant on Clay Minerals, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **71**, 229-307, 1993.
- ¹³¹ M. G. Stapleton, D. L. Sparks, S. K. Dentel, Sorption of Pentachlorophenol to HDTMA-Clay as a Function of Ionic Strength and pH, *Environ. Sci. Technol.*, **28**, 2330-2335, 1994.
- ¹³² M. Sánchez-Camazano, M. J. Sánchez- Martín, Organo-Clays as Adsorbents for Azinphosphomethyl and Dichlorvos in Aqueous Medium, *Water, Air, and Soil Pollution*, **74**, 19-28, 1994.
- ¹³³ R. M. Cornell, Adsorption of Cesium on Minerals: A Review, *J. Radioanalytical and Nuclear Chemistry, Articles*, **171**, 2, 483-500, 1993.
- ¹³⁴ D. W. Oscarson, H. B. Hume, F. King, Sorption of Cesium on Compacted Bentonite, *Clays and Clay Miner.*, **42**, 6, 731-736, 1994.
- ¹³⁵ S. A. Khan, R. U. Rehman, M. A. Khan, Sorption of Cesium on Bentonite, *Waste Management*, **14**, 7, 629-642, 1994.
- ¹³⁶ R. Ramebäck, Y. Albinson, M. Skälberg, L. Werme, Release and Diffusion of ⁹⁰Sr from Spent UO₂ Fuel in Bentonite Clay, *Radiochimica Acta*, **66/67**, 405-408, 1994.
- ¹³⁷ T. Ohnuki, N. Kozai, Sorption Characteristics of Radioactive Cesium and Strontium on Bentonite, *Radiochimica Acta*, **66/67**, 327-331, 1994.
- ¹³⁸ T. E. Payne, J. A. Davis, T. D. Waite, Uranium Retention by Weathered Schists - The Role of Iron Minerals, *Radiochimica Acta*, **66/67**, 297-303, 1994.
- ¹³⁹ M. Ivanovich, A. Hernandez Benitez, A. V. Chambers, S. E. Hasler, Uranium Series Isotopic Study of Fracture Infill Materials from El Berrocal Site, Spain, *Radiochimica Acta*, **66/67**, 485-494, 1994.
- ¹⁴⁰ K. H. Lieser, T. H. Steinkopff, Chemistry of Radioactive Iodine in the Hydrosphere and in the Geosphere, *Radiochimica Acta*, **46**, 49-55, 1989.
- ¹⁴¹ J. Bors, A. Gorny, S. Dultz, Some Factors Affecting the Interactions of Organophilic Clay Minerals with Radioiodine, *Radiochimica Acta*, **66/67**, 309-313, 1994.

-
- ¹⁴² J. Bors, A. Gorny, Studies on the Interactions of HDPY-Vermiculite with Radioiodine, *Appl. Clay Sci.*, **7**, 245-250, 1992.
- ¹⁴³ J. A. Smith, P. R. Jaffe, Comparison of Tetrachloromethane Sorption to an Alkylammonium-Clay and an Alkyldiammonium-Clay, *Environ. Sci. Tech.*, **25**, 2054-2058, 1991.
- ¹⁴⁴ J. A. Raussell-Colom, J. M. Serratosa, Reaction of Clays with Organic Substances, in *Chemistry of Clays and Clay Minerals*, (A. C. D. Newman, Ed.), Longmans, London, 371-422, 1987.
- ¹⁴⁵ H. Kodama, M. Schnitzer, Effects of Interlayer Cations on the Adsorption of a Soil Humic Compound by Montmorillonite, *Soil Sci.*, **106**, 73-74, 1968.
- ¹⁴⁶ R. L. Parfitt, D. J. Greenland, Adsorption of Water by Montmorillonite-Poly(Ethylene Glycol) Adsorption Products, *Clay Miner.*, **8**, 317-324, 1970
- ¹⁴⁷ B. K. G. Theng, D. J. Greenland, J. P. Quirk, Adsorption of Alkylammonium Cations by Montmorillonite, *Clay Miner.*, **7**, 1-17, 1967.
- ¹⁴⁸ E. F. Vansant, J. B. Peeters, The Exchange of Alkylammonium Ions on Na-Laponite, *Clays and Clay Miner.*, **26**, 279-284, 1978.
- ¹⁴⁹ R. E. Grim, W. H. Allaway, F. L Cuthbert, Reaction of Different Clay Minerals with Some Organic Cations, *J. Amer. Chem. Soc.*, **30**, 137-142, 1947.
- ¹⁵⁰ C. T. Cowan, D. White, The Mechanism of Exchange Reactions Occurring Between Sodium Montmorillonite and Various n-Primary Aliphatic Amine Salts, *Trans. Faraday Soc.*, **54**, 691-697, 1958.
- ¹⁵¹ S. Xu, S. A. Boyd, Cation Exchange Chemistry of Hexadecyltrimethylammonium in a Subsoil Containing Vermiculite, *Soil Sci. Soc. Am. J.*, **58**, 1382-1391, 1994.
- ¹⁵² J. T. Kunjappu, P. Somasundaran, Tris(2,2'-bipyridyl)ruthenium (II) Chloride as a Probe of Adsorption Characteristic of Sodium Dodecyl Sulfate on Alumina, *Colloids and Surfaces*, **38**, 305-311, 1989.
- ¹⁵³ G. Lagaly, A. Weiss, Determination of the Layer Charge in Mica-Type Layer Silicates, in *Proc. Inter. Clay Conf., Tokyo*, (L. Heller, Ed.), Israel Univ. Press, Jerusalem, Vol. 1, 61-80, 1969.
- ¹⁵⁴ G. Lagaly, Layer Charge Heterogeneity in Vermiculites, *Clays and Clay Miner.*, **30**, 215-222, 1982.
- ¹⁵⁵ R. M. Barrer, K. E. Kelsey, Thermodynamics of Interlamellar Complexes. 1. Hydrocarbons in Methylammonium Montmorillonites, *Trans. Faraday Soc.*, **57**, 452-462, 1961.

-
- ¹⁵⁶ R. M. Barrer, K. E. Kelsey, Thermodynamics of Interlamellar Complexes. 2. Sorption by Dimethyldioctadecylammonium Bentonite, *Trans. Faraday Soc.*, **57**, 625-640, 1961.
- ¹⁵⁷ A. C. Olis, P. B. Malla, L. A. Douglas, The Rapid Estimation of the Layer Charges of 2:1 Expanding Clays from a Single Alkylammonium Ion Expansion, *Clay Miner.*, **25**, 39-50, 1990.
- ¹⁵⁸ F. Favre, G. Lagaly, Organo-Bentonites with Quaternary Alkylammonium Ions, *Clay Miner.*, **26**, 19-32, 1991.
- ¹⁵⁹ G. Lagaly, A. Weiss, Inhomogeneous Charge Distribution in Mica-Type Layer Silicates, *Réunion Hispano-Belga de Minerales de la Arcilla, Madrid*, 179-187, 1970.
- ¹⁶⁰ G. Lagaly, A. Weiss, The Layer Charge of Smectitic Layer Silicates, in *Proc. Inter. Clay Conf., Mexico City*, (S. W. Bailey, Ed.), Applied Publishing, Wilmette, Illinois, 157-172, 1976.
- ¹⁶¹ J. V. Nye, W. F. Guerin, S. A. Boyd, Heterotrophic Activity of Microorganisms in Soils Treated with Quaternary Ammonium Compounds, *Environ. Sci. Tech.*, **28**, 5, 944-951, 1994.
- ¹⁶² M. J. Geoghegan, R. C. Brian, Influence of Bacterial Polysaccharides on Aggregate Formation in Soils, *Nature*, **158**, 837, 1946.
- ¹⁶³ M. J. Geoghegan, R. C. Brian, Aggregate Formation in Soil. 2. Influence of Various Carbohydrates and Proteins in Aggregation of Soil Particles, *Biochem. J.*, **43**, 5-13, 1948.
- ¹⁶⁴ F. W. Billmeyer, Text book of Polymer Science, John Wiley and Sons, New York, 1984.
- ¹⁶⁵ B. K. G. Theng, Clay-Polymer Interactions: Summary and Perspectives, *Clays and Clay Miner.*, **30**, 1, 1-10, 1982.
- ¹⁶⁶ R. L. Parfitt, D. J. Greenland, Adsorption of Polysaccharides by Montmorillonite, *Soil Sci. Soc. Am. J.*, **34**, 862-866, 1970
- ¹⁶⁷ C. Chenu, C.H. Pons, M. Robert, Interaction of Kaolinite and Montmorillonite with Neutral Polysaccharides, in *Inter. Clay Conf., Denver*, (L. G. Schultz, Ed.), 375-381, 1987.
- ¹⁶⁸ A. Silberg, The Adsorption of Flexible Macromolecules. Part I. The Isolated Macromolecule at a Plane Surface, *J. Phys. Chem.*, **66**, 1872-1883, 1962.
- ¹⁶⁹ J. Y. Bottero, M. Bruant, J. M. Cases, D. Canet, F. Fiessinger, Adsorption of Nonionic Polyacrylamide on Sodium Montmorillonite: Relation Between Adsorption, Zeta Potential, Turbidity, Enthalpy of Adsorption Data and ¹³C-NMR in Aqueous Solution, *J. Coll. Int. Sci.*, **124**, 2, 515-527, 1988.

-
- ¹⁷⁰ N. Schamp, J. Huylebroeck, Adsorption of Polymers on Clays, *J. Polymer Sci.*, **42**, 553-562, 1973.
- ¹⁷¹ D. J. Greenland, Adsorption of Polyvinyl Alcohols by Montmorillonite, *J. Coll. Sci.*, **18**, 647-664, 1963.
- ¹⁷² R. A. Ruehrwain, D. W. Ward, Mechanism of Clay Aggregation by Polyelectrolytes, *Soil Sci.*, **73**, 485-492, 1952.
- ¹⁷³ J. L. Mortensen, Adsorption of Hydrolysed Polyacrylonitrile on Kaolinite; in *Clays and Clay Miner., Proc. 9th Natl. Conf., West Lafayette, Indiana, 1962*, (A. Swineford, Ed.), Pergamon Press, New York, 350-545, 1962.
- ¹⁷⁴ T. Stutzmann, B. Siffert, Contribution to the Adsorption Mechanism of Acetamide and Polyacrylamide onto Clay, *Clays and Clay Miner.*, **25**, 392-406, 1977.
- ¹⁷⁵ D. J. Greenland, Interaction Between Organic Polymers and Inorganic Soil Particles, in *Proc. Symp. Fund. Soil Cond.*, (M. DeBoodt, Ed.), 1972.
- ¹⁷⁶ L. T. Lee, R. Rahbari, J. Lecourtier, G Chauveteau, Adsorption of Polyacrylamides on the Different Faces of Kaolinites, *J. Coll. Int. Sci.*, **147**, 351-357, 1991.
- ¹⁷⁷ P. Espinasse, B. Siffert, Acetamide and Polyacrylamide Adsorption onto Clays: Influence of the Exchangeable Cation and the Salinity of the Medium, *Clays and Clay Miner.*, **27**, 179-284, 1979.
- ¹⁷⁸ M. Ben-Hur, M. Malik, J. Letey, U. Mingelgrin, Adsorption of Polymers on Clays as Affected by Clay Charge and Structure, Polymer Properties and Water Quality, *Soil Science*, **153**, 5, 349-356, 1992.
- ¹⁷⁹ M. M. Mortland, Clay-Organic Complexes and Interactions, *Advan. Agron.*, **22**, 75-117. 1970.
- ¹⁸⁰ R. Denoyel, G. Durand, F. Lafuma, R. Audebert, Adsorption of Cationic Polyelectrolytes onto Montmorillonite and Silica: Microcalorimetric Study of Their Conformation, *J. Coll. Int. Sci.*, **139**, 281-290, 1990.
- ¹⁸¹ A. P. Black, F. B. Birkner, J. J. Morgan, The Effect of Polymer Adsorption on the Electrokinetic Stability of Dilute Clay Complexes, *J. Coll. Int. Sci.*, **21**, 626-648, 1966.
- ¹⁸² T. Ueda, S. Harada, Adsorption of Cationic Polysulfone on Bentonite, *J. Appl. Polymer Sci.*, **12**, 2395-2401, 1968.
- ¹⁸³ B. Gu, H. E. Doner, The Interaction of Polysaccharides with Silver Hill Illite, *Clays and Clay Miner.*, **40**, 2, 151-156, 1992.
- ¹⁸⁴ B. Gu, H. E. Doner, Adsorption of Hydroxy-Al Polycations and Destabilization of Illite and Montmorillonite Suspensions, *Clays and Clay Miner.*, **38**, 5, 493-500, 1990.

-
- ¹⁸⁵ C. Breen, J. O. Rawson, B. E. Mann, Adsorption of Polycations On Clays: an In-Situ Study Using ¹³³Cs Solution-Phase NMR, *J. Mat. Chem.*, **6**, 253-260, 1996.
- ¹⁸⁶ F. Mabire, R. Audebert, C. Quivoron, Floccuation Properties of Some Water Soluble Cationic Copolymers Towards Silica Suspensions: A Semiquantitative Interpretation of the Role of Molecular Weight and Cationicity Through a 'Patchwork' Model, *J. Coll. Int. Sci.*, **97**, 120-136, 1984.
- ¹⁸⁷ T. K. Wang, R. Audebert, Flocculation Mechanisms of a Silica Suspension by Some Weakly Cationic Polyelectrolytes, *J. Coll. Int. Sci.*, **119**, 459-465, 1987.
- ¹⁸⁸ S. Vaslin-Reimann, F. Lafuma, R. Audebert, Reversible Flocculation of Silica Suspensions Through Water Soluble Polymers, *J. Coll. Int. Sci.*, **268**, 476-483, 1990.
- ¹⁸⁹ G. Durand-Piana, F. Lafuma, R. Audebert, Flocculation and Adsorption Properties of Cationic Polyelectrolytes Towards Na-montmorillonite Dilute Suspensions, *J. Coll. Int. Sci.*, **119**, 474-480, 1986.
- ¹⁹⁰ M. A. Cohen Stuart, T. Cosgrove, B. Vincent, Experimental Aspects of Polymer Adsorption at Solid/Solution Interfaces, *Adv. Coll. Int. Sci.*, **60**, 448-465, 1977.
- ¹⁹¹ S. M. Aly, J. Letey, Polymers and Water Quality Effect on Flocculation of Montmorillonite, *Soil Sci. Soc. Am. J.*, **52**, 1453-1458, 1988.
- ¹⁹² J. Letey, Adsorption and Desorption of Polymers on Soil, *Soil Sci.*, **158**, 4, 244-248, 1994.
- ¹⁹³ K. Wong, P. Lixon, F. Lafuma, P. Linder, O. Aguerre Charriol, B. Cabane, Intermediate Structures in Equilibrium Flocculation, *J. Coll. Int. Sci.*, **153**, 55-72, 1992.
- ¹⁹⁴ D. H. Napper, Polymeric Stabilisation of Colloidal Dispersions, Academic Press, London, 1993.
- ¹⁹⁵ J. Gregory, Rates of Flocculation of Latex Particles by Cationic Polymers, *J. Coll. Int. Sci.*, **42**, 448-456, 1972.
- ¹⁹⁶ J. Papenhuijzen, H. A. van der Schee, G. J. Fleer, Polyelectrolyte Adsorption 1. A New Lattice Theory, *J. Coll. Int. Sci.*, **104**, 540, 1985.
- ¹⁹⁷ E. Dickinson, L. Eriksson, Particle Flocculation by Adsorbing Polymers, *Adv. Coll. Int. Sci.*, **34**, 1-29, 1991.
- ¹⁹⁸ C. L. Thomas, J. Hickey, G. Stecker, Chemistry of Clay Cracking Catalysts, *Ind. Eng. Chem.*, **42**, 866-871, 1950.
- ¹⁹⁹ H. Kaplan, One Step Process of Acid Activating Mineral Clays and Alkylating Phenolic Compounds with an Alkene Hydrocarbon, *U. S. Patent*, **3,287,422**, 4, 1966.

-
- ²⁰⁰ F. Hojabri, Dimerisation of Propylene and its Uses for Isoprene Manufacture, *J. Appl. Chem. Biotech.*, **21**, 87-89, 1971.
- ²⁰¹ M. C. Sanchez, J. Garcia, J. A. Mayoral, J. Blasco, M. G. Proietti, Structural Study of Ti^{IV} Exchnaged K-10 Montmorillonite by XRD, EXAFS and XANES, *J. Mol. Catal.*, **92**, 311-324, 1994.
- ²⁰² R. Mokaya, W. Jones, Pillared Acid-Activated Clay Catalysts, *J. Chem. Soc. Chem. Commun.*, 929-930, 1994.
- ²⁰³ J. Bovey, W. Jones, Characterization of Al-Pillared Acid-Activated Clay Catalysts, *J. Mat. Chem.*, **5**, 2027-2035, 1995.
- ²⁰⁴ R. Mokaya, W. Jones, M. E. Davies, M. E. Whittle, Chlorophyll Adsorption by Alumina Pillared Acid-Activated Clays, *J. Am. Oil Chem. Soc.*, **70**, 241-244, 1993.
- ²⁰⁵ A. Hirokawa, Characteristics and Applications of the Acid-Treated 'Acid-Clay', *Nendo Kagaku*, **20**, 99-106, 1980.
- ²⁰⁶ I. Novák, M. Gregor, Surface Area and Decolorizing Ability of Some Acid-Treated Montmorillonites, *Proc. Int. Clay Conf. Tokyo*, 851-857, 1969.
- ²⁰⁷ M. A. Vicente-Rodriguez, M. Suarez-Barrios, J. D. Lopez-Gonzalez, M. A. Bañares-Muñoz, Acid Activation of a Ferrous Saponite (Griffithite): Physico-Chemical Characterization and Surface Area of the Products Obtained, *Clays and Clay Miner.*, **42**, 6, 724-730, 1994.
- ²⁰⁸ G. A. Mills, J. Holmes, E. B. Cornelius, Acid Activation of Some Bentonite Clays, *Phys. Coll. Chem.*, **54**, 1170, 1950.
- ²⁰⁹ W. T. Granquist, G. Gardner-Summer, Acid Dissolution of Texas Bentonite, *Clays and Clay Miner.*, **6**, 292, 1959.
- ²¹⁰ S. Mendioroz, J. A. Pajares, I. Benito, C. Pesquera, F. Gonzales, C. Blanco, Texture Evolution of Montmorillonite Under Progressive Acid Treatment: Change from H3 to H2 type Hysteresis, *Langmuir*, **3**, 676-681, 1987.
- ²¹¹ C. N. Rhodes, D. R. Brown, Structural Characterisation and Optimisation of Acid-Treated Montmorillonite and High Porosity Silica Supports for ZnCl₂ Alkylation Catalysts, *J. Chem. Soc., Faraday Trans.*, **88**, 2269-2274, 1992.
- ²¹² L. Gonzalez, R. L. Ibarra, D. A. Rodriguez, Preparation of Silica by Acid Dissolution of Sepiolite and Study of its Reinforcing Effect in Elastomers, *D. Angew Makromol. Chemie*, **103**, 51-60, 1982.
- ²¹³ J. L. Acosta, C. M. Rocha, M. C. Ojeda, The Effect of Several Modified Sepiolites on the Transition Temperatures and Crystallinity of Filled Propylene, *D. Angew Makromol. Chemie*, **126**, 51-57, 1984.

-
- ²¹⁴ A. Corma, J. Perez-Pariente, V. Fornes, A. Mifsud, Catalytic Activity of Modified Smectites: I Dehydration of Ethanol Catalysed by Acidic Sepiolite, *Clays and Clay Miner.*, **19**, 207-215, 1984.
- ²¹⁵ B. Cícel, I. Novák, Dissolution of Smectites in Hydrochloric Acid. I. Half-Time of Dissolution as a Measure of the Reaction Rate, in *Proc. 7th Conf., Clay Miner. Petrol.*, (J. Konta, Ed.), Charles Univ., Prague, 163-171, 1977.
- ²¹⁶ I. Novák, B. Cícel, Dissolution of Smectites in Hydrochloric Acid. II. Dissolution as a Function of Crystallochemical Composition, *Clays and Clay Miner.*, **26**, 341-344, 1978.
- ²¹⁷ J. Madejová, E. Bednáriková, P. Komadel, B. Cícel, Structural Study of Acid-Treated Smectites By IR Spectroscopy, in *Proc. 11th Conf. Clay Miner. Petrol.*, (C. Budejovice, Ed.), 267-271, 1993.
- ²¹⁸ C. Breen, J. Madejová, P. Komadel, Correlation of Catalytic Activity with Infra-Red, ²⁹Si MAS NMR and Acidity Data for HCl-Treated Fine Fractions of Montmorillonites, *Appl. Clay Sci.*, **10**, 219-230, 1995.
- ²¹⁹ C. Breen, J. Madejová, P. Komadel, Characterisation of Moderately Acid-Treated, Size-fractionated Montmorillonites using IR and MAS NMR Spectroscopy and Thermal Analysis, *J. Mater. Chem.*, **5**, 3, 469-474, 1995
- ²²⁰ M. A. Vicente-Rodriguez, M. Suarez-Barrios, J. D. Lopez-Gonzalez, M. A. Bañares-Muñoz, Characterisation, Surface Area, And Porosity Analysis of the Solids Obtained by Acid Leaching of a Sapomite, *Langmuir*, **12**, 566-572, 1996.
- ²²¹ P. Komadel, J. Madejová, M. Janek, W. P. Gates, R. J. Kirkpatrick, J. W. Stucki, Dissolution of Hectorite in Inorganic Acids, *Clays and Clay Miner.*, **44**, 228-236, 1996.
- ²²² V. Luca, D. J. MacLachlan, Site Occupancy in Nontrite Studied by Acid Dissolution and Mössbauer Spectroscopy, *Clays and Clay Miner.*, **40**, 1-7, 1992.
- ²²³ M. Janek, P. Komadel, Autotransformation of H-Smectites in Aqueous Solution, The Effect of Octahedral iron Content, *Geol. Carpath. Ser. Clays*, **44**, 59-64, 1993.
- ²²⁴ C. Breen, The Acidity of Trivalent Cation-Exchanged Montmorillonite. II. Desorption of Mono- and Di- Substituted Pyridines, *Clay Miner.*, **23**, 323-328, 1988.
- ²²⁵ N. Jovanovic, J. Janackovic, Pore Structure and Adsorption Properties of an Acid Activated Bentonite, *Appl. Clay Sci.*, **6**, 59-68, 1991.
- ²²⁶ N. T. Coleman, D. Craig, The Spontaneous Alteration of Hydrogen Clay, *Soil Sci.*, **91**, 14-18, 1961.

-
- ²²⁷ I. Barshad, A. E. Foscolos, Factors Affecting the Rate of the Interchange Reaction of Adsorbed H⁺ on the 2:1 Clay Minerals, *Soil Sci.*, **110**, 52-60, 1970.
- ²²⁸ C. N. Rhodes, D. R. Brown, Autotransformation and Ageing of Acid-Treated Montmorillonite Catalysts: A Solid-State ²⁷Al NMR Study, *J. Chem. Soc., Faraday Trans.*, **91**, 6, 1031-1035, 1995.
- ²²⁹ L. E. Davis, R. Turner, L. D. Whittig, Some Studies of the Autotransformation of H-Bentonite to Al-Bentonite, *Soil Sci. Soc. Proc.*, **26**, 441-443, 1962.
- ²³⁰ A. Banin, S. Ravikovitch, Kinetics of Reactions in the Conversion of Na- or Ca-Saturated Clay to H-Al Clay, *Clays and Clay Miner.*, **14**, 193-204, 1966.
- ²³¹ R. P. Mitra, B. S. Kapoor, Acid Character of Montmorillonite: Titration Curves in Water and Some Non-Aqueous Solvents, *Soil Sci.*, **108**, 11-23, 1969.
- ²³² M. T. Kaddah, N. T. Coleman, Salt Displacement of Acid-Treated Trioctahedral Vermiculites, *Soil Sci. Soc. Amer. Proc.*, **31**, 333-336, 1967.
- ²³³ R. W. Luce, R. W. Bartlett, G. A. Parks, Dissolution Kinetics Of Magnesium Silicates, *Geochimica et Cosmochimica Acta*, **36**, 35-50, 1972.
- ²³⁴ N. M. Rice, L. W. Strong, The Leaching of Latritic Nickel Ores in Hydrochloric Acid, *Canadian Metallurgical Quarterly*, **b13**, 485-493, 1974.
- ²³⁵ D. W. Johnson, F. A. Peters, R. C. Kirby, Methods for Producing Alumina from Clay, *Bur. Mines Rep. Invest.*, **27**, 6431, 1-25, 1964.
- ²³⁶ A. Corma, A. Mifsud, E. Sanz, Influence of the Chemical Composition and Textural Characteristics of Palygorskite on the Acid Leaching of Octahedral Cations, *Clays Miner.*, **22**, 225-232, 1987.
- ²³⁷ R. Fahn, Influence of the Structure and Morphology of Bleaching Earths on Their Bleaching Action on Oils and Fats, *Fette, Seifen, Anstrichmit.*, **75**, 77-82, 1973,
- ²³⁸ H. Kaviratna, T. J. Pinnavaia, Acid Hydrolysis of Octahedral Mg²⁺ Sites in 2:1 Layered Silicates: An Assessment of Edge Attack and Gallery Access Mechanisms, *Clays and Clay Miner.*, **42**, 6, 717-723, 1994.
- ²³⁹ H. Cetisli, T. Gedikbev, Dissolution Kinetics of Sepiolite from Eskisehir (Turkey) in Hydrochloric and Nitric Acids, *Clay Miner.*, **25**, 207-215, 1990.
- ²⁴⁰ S. Bodoardo, F. Figueras, E. Garrone, IR Study of Brønsted Acidity of Al-Pillared Montmorillonite, *Journal of Catalysis*, **147**, 223-230, 1994.
- ²⁴¹ C. Güler, N. Sarier, Kinetics of the Thermal Dehydration of Acid-Activated Montmorillonite by the Rising Temperature Technique, *Thermochim. Acta*, **159**, 29-33, 1990.

-
- ²⁴² M. Garcia, J. R. Gancedo, J. F. Marco, M. J. Franco, S. Mendioroz, J. A. Pajares, Mössbauer Study of Iron Removal in a Montmorillonite, *Hyperfine Interactions*, **46**, 629-634, 1989.
- ²⁴³ J. Ravichandran, B. Sivasankar, Characterization of Acid Activated Montmorillonite and Vermiculite Clays by Thermal Desorption and Differential Scanning Calorimetric Techniques, *Indian Journal of Chemistry*, **13A**, Feb., 127-130, 1995.
- ²⁴⁴ V. C. Farmer, The Infrared Spectra of Minerals, The Mineralogical Society, (V. C. Farmer, Ed.), London, 331-363, 1974.
- ²⁴⁵ N. T. Coleman, G. W. Thomas, Basic Chemistry of Soil Acidity: In *Soil Acidity and Liming*, (R. W. Pearson and F. Adams, Eds.), Amer. Soc. Agron. Madison, Wisconsin, 1-41, 1967.
- ²⁴⁶ R. H. Loeppert, L. W. Zelazny, B. G. Volk, Titration of pH-Dependant Sites of Kaolinite in Water and Selected Nonaqueous Solvents, *Clays and Clay Miner.*, **27**, 57-62, 1979.
- ²⁴⁷ C. I. Rich, Conductometric And Potentiometric Titrations of Exchangeable Aluminium, *Soil Sci. Soc. Amer. Proc.*, **34**, 31-38, 1970.
- ²⁴⁸ J. A. Ballantine, The Reaction in Clays and Pillared Clays, in *Chemical Reactions in Organic and Inorganic Constrained Systems*, (R. Button. Ed.), Reidel, Dordrecht, 197-212, 1986.
- ²⁴⁹ J. A. Ballantine, M. Davies, J. Patel, J. H. Purnell, M. Rayanakorn, K. J. Williams, J. M. Thomas, Organic Reactions Catalysed by Sheet Silicates: Ether Formation by Intermolecular Dehydration of Alcohols and by Addition of Alcohols to Alkenes, *J. Mol. Catal.*, **26**, 37-56, 1984.
- ²⁵⁰ G. W. Brindley, R. E. Semple, Preparation and Properties of some Hydroxy-Aluminium Beidellites, *Clay Miner.*, **12**, 229-236, 1977.
- ²⁵¹ M. Lahav, U. Shani, J. Shabtai, Cross-Linked Smectites. I. Synthesis and Properties of Hydroxy-Aluminium Montmorillonites, *Clays and Clay Miner.*, **26**, 105-115, 1978.
- ²⁵² D. E. W. Vaughan, R. G. Lussier, J. S. Magee, Jr., Pillared Interlayered Clay Materials Useful as Catalysts and Sorbents: *U. S. Patent* 4,176,090, Nov. 27, 1979.
- ²⁵³ M. L. Occelli, P. M. Tindwa, Physicochemical Properties of Montmorillonite Interlayered with Cationic Oxyaluminium Pillars, *Clays and Clay Miner.*, **31**, 22-28, 1983.
- ²⁵⁴ E. Kikuchi, T. Matsuda, Shape Selective Acid Catalysis by Pillared Clays, *Catal. Today*, **2**, 297-307, 1988.

-
- ²⁵⁵ J. M. Thomas, Uniform Heterogeneous Catalysts: The Role of Solid State Chemistry in Their Development and Design, *Angew. Chem.*, **27**, 1973-1991, 1988.
- ²⁵⁶ R. A. Schoonheydt, Clays: From Two to Three Dimensions: in *Introduction to Zeolites: Science and Practise*, (H. Van Bekkum, E. M. Flanigen, J. C. Jansen, Eds.), Elsevier, Amsterdam, 201-239, 1991.
- ²⁵⁷ He Ming-Yuan, L. Zhonghui, M. Enze, Acidic and Hydrocarbon Catalytic Properties of Pillared Clays: *Catal. Today*, **2**, 321-338, 1988.
- ²⁵⁸ F. Figueras, Pillared Clays as Catalysts, *Catal. Rev. Sci-Eng.*, **30**, 457-499, 1988.
- ²⁵⁹ D. T. B. Tennakoon, W. Jones, J. M. Thomas, J. A. Ballantine, J. H. Purnell, Characterisation of Clay and Pillared Clay Catalysts, *Solid State Ionics*, **24**, 205-212, 1987.
- ²⁶⁰ S. A. Zubkov, L. M. Kustov, V. B. Kazansky, G. Fetter, D. Tichit, F. Figueras, Study of the Nature of Acid Sites of Montmorillonites Pillared with Aluminium and Oligosilsesquioxane Complex Cations. 1. Brønsted Acidity, *Clays and Clay Miner.*, **42**, 4, 421-427, 1994.
- ²⁶¹ F. Kooli, J. Bovey, W. Jones, Dependence of the Properties of Titanium-Pillared Clays on the Host Matrix, A Comparison of Montmorillonite, Saponite and Rectorite Pillared Materials, *J. Mat. Chem.*, **7**, 153-158, 1997.
- ²⁶² J. Bovey, F. Kooli, W. Jones, Preparation and Characterization of Ti-Pillared Acid-Activated Clay Catalysts, *Clay Miner.*, **31**, 501-506, 1996.
- ²⁶³ J. Bovey, E. Fowles, W. Jones, R. Mokaya, M. E. Davies, GB Patent No. PCT/GB94/02480.
- ²⁶⁴ R. Mokaya, W. Jones, M. E. Whittle, M. E. Davies, Synthesis and Characterization of Pillared Acid-Activated Montmorillonites, *Mat. Res. Soc. Symp. Proc.*, **233**, 81-88, 1991.
- ²⁶⁵ R. Mokaya, W. Jones, Pillared Clays and Pillared Acid-Activated Clays: A Comparative Study of Physical, Acidic, and Catalytic Properties, *J. Catal.*, **153**, 76-85, 1995.
- ²⁶⁶ J. Sterte, Synthesis and Properties of Titanium Oxide Cross-Linked Montmorillonite, *Clays and Clay Miner.*, **34**, 658-664, 1986.
- ²⁶⁷ H. Yoneyama, S. Haga, S. Yanamaka, Photocatalytic Activities of Microcrystalline TiO₂ Incorporated in Sheet Silicates of Clay, *J. Phys. Chem.*, **93**, 4833-4837, 1989.
- ²⁶⁸ J. Bovey, Modified Layered Silicates as Acid Catalysts, PhD Thesis, Univ. Cambridge, UK, 1996.
- ²⁶⁹ J.-T. Lin, S.-J. Jong, S. Cheng, A New Method for Preparing Microporous Titanium Pillared Clays, *Microporous Mater.*, **1**, 287-290, 1993.

-
- ²⁷⁰ C. N. Rhodes, D. R. Brown, Catalytic Activity of Acid Treated Montmorillonite in Polar and Non-Polar Reaction Media, *Catal. Lett.*, **24**, 285-291, 1994.
- ²⁷¹ D. J. Charles, J. E. Simon, Volatile Compounds of the Curry Plant, *Hortscience*, **26**, 69-70, 1991.
- ²⁷² P. A. Wender, N. F. Badham, S. P. Conway, P. E. Floreancig, T. E. Glass, J. B. Houze, N. E. Krauss, D. Lee, D. G. Marquess, P. L. McGrane, W. Meng, T. P. Mucciaro, M. Mühlbach, M. G. Natchus, T. Ohkuma, B. Peschke, D. B. Rawlins, A. J. Shuker, J. C. Sutton, R. E. Taylor, K. Tomooka, L. A. Wessjohann, The Pinene Path to Taxanes, *A.C.S. Symp. Series*, **583**, 326-339, 1995.
- ²⁷³ J. C. Schmidhauser, G. L. Bryant, Jr., P. E. Donahue, M. F. Garbauskas, E. A. Williams, Products from the Acid-Catalysed Reaction of Cyclic Monoterpenes and Phenol, *J. Org. Chem.*, **60**, 3612-3618, 1995.
- ²⁷⁴ H. Hennig, J. Behling, R. Meusinger, L. Weber, Photocatalytic Oxygenation of Selected Cycloalkenes in Aqueous Solutions Induced by Water-Soluble Metal Porphyrin Complexes, *Chem. Ber.*, **128**, 229-234, 1995.
- ²⁷⁵ C. M. Williams, D. Whittaker, Rearrangements of Pinane Derivatives. Part I. Products of Acid Catalysed Hydration of α -Pinene and β -Pinene, *J. Chem. Soc. (B)*, 668-672, 1971.
- ²⁷⁶ C. M. Williams, D. Whittaker, Rearrangements of Pinane Derivatives. Part II. Products of Acid Catalysed Hydration of α -Pinene and β -Pinene in Acetic Acid, *J. Chem. Soc. (B)*, 672-677, 1971.
- ²⁷⁷ A. Severino, J. Vital, L. S. Lobo, Isomerisation of α -Pinene over TiO₂: Kinetics and Catalyst Optimisation, *Heterogeneous Catalysis and Fine Chemicals III*, **78**, 685-692, 1993.
- ²⁷⁸ A. De Stefanis, G. Perez, O. Ursini, A. A. G. Tomlinson, PLS versus Zeolites as Sorbents and Catalysts II. Terpene Conversions in Alumina-Pillared Clays and Phosphates and Medium Pore Zeolites, *Applied Catalysis A: General*, **132**, 353-365, 1995.
- ²⁷⁹ J. C. van der Waal, H. van Bekkum, J. M. Vital, The Hydration and Isomerization of α -Pinene over Zeolite Beta. A New Coupling Reaction Between α -Pinene and Ketones, *J. Mol. Catal. A: Chemical*, **105**, 185-192, 1996.
- ²⁸⁰ M. C. Cruz-Costa, R. A. W. Johnstone, D. Whittaker, Catalysis of Gas and Liquid Phase Ionic and Radical Rearrangements of α - and β -Pinene by Metal (IV) Phosphate Polymers, *J. Mol. Catal. A: Chemical*, **104**, 251-259, 1996.
- ²⁸¹ V. Krishnasamy, P. Mathur, K. Balasubramanian, Ensembling Parameters for the Dehydrogenation of 3-Carene, α -Pinene, β -Pinene and Camphene Over Platinum-Alumina Catalyst, *Chem. Eng Commun.*, **23**, 115-123, 1983.

-
- ²⁸² A. Banin, N. Lahav, Particle Size and Optical Properties of Montmorillonite in Suspension, *Israel J. Chem.*, **6**, 235-250, 1968.
- ²⁸³ L. Bailey, M. Keall, A. Audibert, J. Lecourtier, The Effect of Clay/Polymer Interactions on Shale Stabilization During Drilling, *Langmuir*, **10**, 5, 1994.
- ²⁸⁴ D. R. Collins, A. N. Fitch, C. Richard, A. Catlow, Dehydration of Vermiculites and Montmorillonites: A Time Resolved Powder Neutron Diffraction Study, *J. Mater. Chem.*, **2**, 865-873, 1992.
- ²⁸⁵ J. Billingham, C. Breen, J. Yarwood, Adsorption of Polyamine, Polyacrylic Acid and Polyethylene Glycol on Montmorillonite: An In-situ Study Using ATR-FTIR, *Vibrational Spectroscopy*, **14**, 19-34, 1997.
- ²⁸⁶ M. B. McBride, T. J. Pinnavaia, M. M. Mortland, Fate of Pollutants in the Air and Water Environments, Wiley and Sons, New York, Part I, 145, 1977.
- ²⁸⁷ S. Brunauer, P. H. Emmett, E. Teller, Adsorption of Gases in Multi-Molecular Layers, *J. Am. Chem. Soc.*, **60**, 309-319, 1938.
- ²⁸⁸ M. B. McBride, M. M. Mortland, Segregation and Exchange Properties of Alkylammonium Ions in a Smectite and Vermiculite, *Clays and Clay Miner.*, **21**, 323-329, 1973.
- ²⁸⁹ M. M. Mortland and T. J. Pinnavaia, Formation of Copper (II)-Arene Complexes on the Interlamellar Surfaces of Montmorillonite, *Nature Phys. Sci.*, **229**, 75-77, 1971.
- ²⁹⁰ T. J. Pinnavaia, M. M. Mortland, Interlamellar Metal Complexes of Layer Silicates. I. Copper (II)-Arene Complexes on Montmorillonite, *J. Phys. Chem.*, **75**, 3957-3962, 1971.
- ²⁹¹ J. Billingham, C. Breen, J. Yarwood, In-Situ Determination of Brønsted/Lewis Acidity on Cation-Exchanged Clay Mineral Surfaces by ATR-IR, *Clay Miner.*, **31**, 513-522, 1997.
- ²⁹² S. A. Boyd, Adsorption of Substituted Phenols by Soil, *Soil Science*, **134**, 337-343, 1982.
- ²⁹³ S. B. Haderlein, R. P. Schwarzenbach, Sensing Reactive Mineral Surfaces in Natural Sediments by Nitroaromatic Model Compounds, in *Transport and Reactive Processes in Aquifers*, (M. Dracos and T. Stauffer, Eds.), 67-72, 1994.
- ²⁹⁴ C. Breen, F. D. Zahoor, J. Madejovà, P. Komadel, Characterisation and Catalytic Activity of Acid-Treated, Size-Fractionated Smectites, *J. Phys Chem.*, 1997, in press.
- ²⁹⁵ J.-Q. Yu, P. Zhou, S.-D. Xiao, Highly Selective Hydration Reaction of α -Pinene Over H-Mordenites Pretreated with Quaternary Ammonium Salts, *Chinese J. Chem.*, **13**, 280-283, 1995.

-
- ²⁹⁶ S. Kullaj, Effect of the Characteristics of Activated Clays and Their Ability to Lead to Isomerism of α -Pinene into Camphene and Tricyclene, *Bull. Shkencave Nat.*, **43**, 81-86, 1989.
- ²⁹⁷ B. Cícel, P. Komadel, S. Lego, J. Madejovà, L. Vlakovà, Iron-Rich Beidellite in the Fine Fraction of Stebno Bentonite, *Geol. Carpath. Ser. Clays*, **44**, 121-126 1993.
- ²⁹⁸ I. Tkáč, P. Komadel, D. Muller, Acid-treated Montmorillonites - A Study by ^{29}Si and ^{27}Al MAS NMR, *Clay Miner.*, **29**, 11-19, 1994.