The synthesis and characterisation of novel long chain dimethyl siloxane surfactants.

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THE SYNTHESIS AND CHARACTERISATION OF NOVEL LONG-CHAIN DIMETHYL SILOXANE SURFACTANTS

by

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Abstract

A basic introduction to liquid crystals and surfactants has been given, along with a description of the main techniques employed in the study of liquid crystals (in particular optical polarising microscopy, differential scanning calorimetry, nuclear magnetic resonance spectroscopy and x-ray diffraction studies).

Conventional surfactants comprise a polar head group and a hydrophobic, hydrocarbon chain ie. they are amphiphilic. Because long chains have high melting points the length of the alkyl chain in these compounds is limited to $\leq$ ca C_{18}, as long chain surfactants are usually insoluble. Therefore, in this project the alkyl group has been replaced by a long, hydrophobic polydimethylsiloxane chain. Polydimethylsiloxanes are low melting materials (glass transition at ca -120°C) with very flexible chains, hence surfactants based on them might be readily soluble in water.

This project involves chemical attachment of amphiphilic mesogens to α - SiH terminated siloxanes of varying lengths and the examination of their surfactant properties. The following type of structure was successfully synthesised:

$CH_3CH_2CH_2CH_2(Si(CH_3)_2O)_n\ Si(CH_3)_2$ - m where
n=integer;
m=amphiphilic mesogen

The amphiphilic head groups of these novel surfactants contained the salts of either a mono-, or a dicarboxylic acid. After the synthesis of these surfactants, the liquid crystal and micelle properties of the sodium and calcium salts, were investigated utilising a number of physical techniques eg. optical microscopy and differential scanning calorimetry.

Finally, some work on synergism has been described. When different types of surfactants are purposely mixed, what is sought is synergism, the condition when the properties of the mixture are better than those attainable with the individual components by themselves.

Acknowledgements

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CONTENTS

PAGE NO.

1. Introduction

Liquid crystals are highly anisotropic fluids that exist between the boundaries of the solid and conventional, isotropic liquid phase. Surfactants (described later) are specific examples of liquid crystals.

The phenomenon of mesomorphism, the formation of a liquid crystalline phase, was first recognised by the Austrian scientist, R. Reinitzer in 1888 (1). He observed that when cholesteryl benzoate is heated it changes to a turbid fluid phase at 146°C and then to a clear liquid at 178.5°C. It was, however, Lehmann (2) who termed this compound a 'Liquid Crystal' because at temperatures greater than 146°C and less that 178.5°C it possessed low rigidity (a liquid-like property), and also optical anisotropy (a crystal-like property).

Materials exhibiting this behaviour remained scientific curiosities until around the 1960s, when device physicists recognised that the unique physical properties associated with liquid crystalline phases could be utilised in a variety of applications. However, the major revolution in the use of liquid crystals came in 1973 with the discovery by Gray, Harrison and Nash of the cyanobiphenyls (3), and the evaluation of their properties at the Royal Signals and Radar Establishment (4). For the first time, one group of mesogens combined the properties needed to produce reliable liquid crystal displays, such as low threshold voltage, fast switching times, and chemical and photochemical stability. Many thousand organic substances and some polymers are now known to exhibit liquid crystallinity (5,6).

Conventionally, matter exists in one of three distinct states of aggregation: the solid state, where constituent molecules have long range order and very little mobility; the liquid state, characterised by no long range structure and little short range order, but rapid molecular motions and some mobility; and the gaseous state. The melting of normal solids involves the abrupt collapse of the overall positional order of the lattice array and marks the onset of essentially free rotation of the particles, although short-range correlations of the position and orientation of molecules occur in the liquid phase. Solids of mesogenic (liquid-crystal forming) molecules melt to form fluids with both long range orientational order and some degree of fluidity (7).

Liquid crystals can be divided into two broad categories according to the principal means of breaking down the complete order of the solid state:

(1) Lyotropic liquid crystals result from the action of a solvent and, hence, are multicomponent mixtures.

(2) Thermotropic liquid crystals result from the melting of mesogenic solids and, hence, are thermally activated mesophases.

Lytotropic liquid crystals are made up of two or more components (8-10). Generally, one of the components is an amphiphile (containing a polar head group attached to one or more long hydrocarbon chains) and the other is water. The most familiar example of a lyotropic liquid crystal is soap (eg. sodium dodecylsulphate) in water. However, lyotropic liquid crystals occur abundantly in nature, particularly in all living systems.

Lyotropic liquid crystals can be divided into categories according to their structure. There is not universal agreement but it is generally accepted that there are four classes of mesophase, these being lamellar, hexagonal, cubic and nematic. The evidence for these structures comes from x-ray and neutron diffraction, optical and electron microscopy, and various spectroscopic methods particularly nuclear magnetic resonance (11-14).

Starting with water and the crystalline form of the surfactant amphiphile, the series of lyotropic liquid crystals can be generated. The mesophases form in the following order as the concentration of surfactant in solution increases:

Water --L_1 --I_1 --H_1 -- V_1 --L_α --V_2 --H_2 --I_2 --L_2 -- Solid
These are described:

L_1	Dilute micellar solution
I_1	Cubic
H_1	Hexagonal (normal)
V_1	Cubic (bicontinuous)
L_α	Lamellar
V_2	Reversed cubic (bicontinuous)
H_2	Reversed hexagonal
I_2	Reversed cubic
L_2	Concentrated surfactant solution

It is worthwhile to point out that this series also shows the order of change in radius of curvature, that is to say, from high radius of curvature through zero (lamellar) to reversed curvature.

Which type of phase is formed depends on many factors, such as concentration of surfactant, packing constraints and temperature. One of the most important, however, is micelle shape (see later). As the chain branching and surfactant mix affects the micelle shape, so in turn this affects the type of mesophase formed. For example, spherical micelles form cubic, then hexagonal, then lamellar phases when the concentration is increased; rod shaped micelles form hexagonal then lamellar phases; disc or bilayer type micelles are likely to form a lamellar phase only.

It is noted that, in addition to the mesophases mentioned above, various intermediate and gel phases are found in some systems, which do not fall into the standard classifications.

The lamellar phase (L_α), also known as the neat phase, is by far the most common for lyotropic liquid crystals. It consists of surfactant bilayers separated by water layers (Fig.1). The surfactant layers have the same average thickness and extend over a large distance, typically a micron or more, and thus have very high aggregation numbers. The width of each layer is dependent upon the overall composition, with the surfactant bilayer thickness being in the region of 0.8 - 1.6 times the all-trans surfactant chain length (L_t). The variation in water layer thickness is considerably greater, in the range 2-200Å, and increases with increased water content. The lamellar phase may also contain defects filled with water ('holes') within the bilayers (15).

The hexagonal phase is the next most common structure. There are two types of hexagonal phase termed normal (H_1) and reversed (H_2). Normal hexagonal, also termed the middle phase, consists of long rod shaped micelles of circular cross section. They are packed in a hexagonal array with water and ions occupying the spaces between the rods (Fig.2). The circular cross section has a diameter of between 1.5 and 2.0 L_t, while the intermicellar separation is in the range 8-50Å (again increasing with water concentration). The reversed hexagonal phase consists of hexagonally packed water cylinders in an alkyl chain continuum. The diameter of the water cylinders is typically 10-20Å, while the separations between the rods is approximately 1.5 L_t (16).

Both L_α and H_1/H_2 are uniaxial, possessing a single axis of symmetry, and are optically anisotropic.

The cubic phases are observed far less frequently than the previously discussed mesophases. They usually occur over a narrow range of temperatures and composition. While it is certain that two very distinct classes of cubic phases occur, their exact structures remain to be fully elucidated. One class of cubic phase (I_1/I_2) occurs at compositions between micellar solutions (L_1/L_2) and hexagonal phases (H_1/H_2). These cubic phases consist of small, usually spherical micelles arranged in primitive, body-centred, or face-centred cubic arrays (Fig.3). While I_1 phases have been observed in many systems, examples of the I_2 phase are rare. The second group of cubic phases (V_1/V_2) is formed at compositions between lamellar (L_α) and hexagonal phases (H_1/H_2). Two different varieties are known to exist (17,18), however, the exact structures remain to be solved. It is thought that they consist of a three-dimensional bicontinuous network with both surfactant and water forming continuous zones (19). Several structures appear to be possible. Translational diffusion coefficients are large for both water and surfactant compared with I_1 cubics which have a much reduced value for the surfactant (20,21). Exact structures of both I and V cubic phases have not been fully elucidated and therefore, this is a very active research area at present (eg. 22-25).

All of the above phases are viscous, with the viscosity usually increasing as follows: $L_\alpha < H_2 < H_1 < V_1 = V_2 < I_1$. The lamellar phase is the only one that can flow under the influence of gravity. As previously mentioned, the lamellar and hexagonal phases are optically anistropic; the cubic phases however, are optically isotropic.

The lyotropic nematic phases resemble the thermotropic nematic phases (described later). The first report of a nematic lyotropic phase was in 1967 (26), and since then extensive studies on their structures have been carried out, particularly by Reeves (27). They occur in a minority of surfactant/water systems between L_1 and H_1 or between L_1 and L_α phases, the most frequent reports being for short chain surfactants (C_n, $n < 14$). Lyotropic nematics are phases that can be aligned in a magnetic field and are optically birefringent. They are mostly uniaxial with fundamental units of aggregates rather than individual molecules, however, a few cases of biaxial nematics have been reported (28). The uniaxial phases consist of either ordered small cylindrical micelles (N_c) or ordered small disc micelles (N_D) (29-32). The structure of the biaxial phases are unknown. The viscosity of the nematic phases is much lower than that of the other lyotropic mesophases.

As previously mentioned, other structures (ie. gel and intermediate phases) are found. At temperatures below those at which lamellar phases occur, surfactant 'gels' are formed in some systems (33-35). Gel phases (L_B) are closely related to the lamellar phase, as both have a layered structure of alternating hydrocarbon and water regions (Fig.4). However, the structure of the gel phase differs with respect to its rigid all-trans alkyl chains, the only motion being rotation about the long axes. Gel phases occur at temperatures below the other mesophases and on heating they usually melt to give lamellar phases, accompanied by a large melting enthalpy. Their stability arises from short range attractions between the alkyl chains. However, it is thought that headgroup interactions also play a significant role (it is likely that strong headgroup interactions promote crystalline phases rather than gels). A specific example of a gel phase is formed by lecithin in water.

Luzzati (36) first reported the existence of intermediate birefringent mesophases, in 1960. Intermediate phases occur between the boundaries of the mesophases described above. Their structures have not yet been fully elucidated but it is thought that there are three distinct classes of intermediate phases, based on rod structures (similar to H_1), layer structures (L_α types) and three dimensional networks (V types).

Lyotropic liquid crystals have proved useful in many commercial applications. In fact they have occurred in the manufacture of soap over thousands of years and are now utilised in many commercial detergents. They are also used in the food industry as emulsifiers. Another area where lyotropic liquid crystals are of interest is their application in biological systems. Liquid crystalline order of amphiphilic molecules occurs in membranous structures such as myelin, cell membranes and chloroplasts.

Other amphiphiles present in biological systems include lecithin, sphingomyelin, and various cerebrosides and gangliosides (37). Ringsdorf (38,39) and Kunitake (40) have recently synthesised polymerisable lipids which may be used to model biomembranes. The reason for the research interest in this particular field is the use of these polymer liposomes as models for the liposome-protein interaction and their application as carriers of drugs and other biologically active substances to the cell.

Thermotropic liquid crystals are formed from compounds (predominantly organic, but also organometallic) whose molecules are mainly either rod-shaped or disc-shaped, either by heating the crystalline solid or by cooling the isotropic liquid, ie. by thermal effects. The liquid crystalline phases have less order than the pure crystal, but more order than the liquid. The chemical characteristics necessary to produce liquid crystalline states have been reviewed by Gray and Winsor (41), and by Brown and Shaw (42). The physical properties of liquid crystals have been reviewed by de Gennes (43).

Following the nomenclature proposed originally by Friedal (44), thermotropic liquid crystals are classified broadly into three types: nematic, cholesteric and smectic.

The nematic liquid crystal mesophases are so called because of the threadlike lines seen in certain preparations (Greek nema = thread). They have a high degree of long range orientational order of the molecules, but no long range translational order (Fig.5). Thus the nematic phase differs from the isotropic liquid in that the molecules are spontaneously orientated into domains with long axes approximately parallel. The preferred direction usually varies from point to point in the medium, but a homogenously aligned specimen is optically uniaxial, positive and strongly birefringent. The mesophase owes its fluidity to the ease with which the molecules slide past one another while still retaining their parallelism. When an electrical potential is applied across a thin film of a nematic phase sandwiched between conducting plates, the molecules undergo changes in orientation which depend on whether their permanent dipoles are parallel or at an angle to the main molecular axis, and on the flow of ions between the plates. The effects have been used as the basis for a number of digital display and optical screening devices. Compounds or mixtures that are nematic at room temperature are required eg. N - (p-methoxybenzylidene) - p - butylaniline.

Cholesteric mesophases are so called because many of the original compounds concerned were derivatives of cholesterol. This state was first described by Reinitzer for his cholesteryl ester (1). The structure can be described as that of a nematic phase twisted about an axis normal to the long axes of the molecules (Fig.6), the pitch of the twist being usually of the order of the wavelength of visible light. As a result of this structure, such phases have very special optical properties, including a very strong optical activity (rotation of the plane of polarised light) along the axis of the twist, which is the optic axis of the medium. The optical sign is negative, because the long molecules (which in cholesteryl derivatives are also considerably flattened) are orientated in all directions normal to the axis of twist over very short intervals along this axis, and this gives the medium similar optical properties to those of a parallel arrangement of planar molecules. Compounds forming cholesteric phases contain molecular asymmetry.

In smectic mesophases the molecules are parallel or approximately parallel to one another, and are grouped into layers with the mean direction of the long axes of the molecules normal to the layers. The term 'smectic' is used because the soaps (salts, mainly Na and K, of long-chain fatty acids) form liquid crystals of this type (Greek smegma = soap). There are many known smectic structures. In smectic A the molecules are upright in each layer with their centres irregularly spaced in a 'liquid-like' fashion (Fig.7). The thickness of the layer is of the order of the length of the free molecule. The interlayer attractions are weak as compared with the lateral forces between molecules and in consequence the layers are able to slide over one another relatively easily. Thus the mesophase has fluid properties, though as a rule it is very much more viscous than the nematic mesophase. Smectic B differs from A in that the molecular centres in each layer are hexagonal close packed. Smectic C is a tilted form of Smectic A, ie. the molecules are inclined with respect to the layers (Fig.8). At least four other distinct smectic modifications have been identified (45,46) but their structures are not yet known with any certainty. Smectic D has been reported to be cubic (47) and would appear to be an exception to the rule that smectics have well defined stratifications.

From purely geometrical arguments, Herrmann (48) concluded that there should be 18 distinct mesomorphic groups between the perfectly ordered crystalline arrangement and the truly amorphous one. Examples of some of these groups have been found in plant virus preparations (49) and in surfactant - water compositions (50), but it is not yet clear whether in fact all of them can give rise to energetically feasible configurations. Thus Friedel's nomenclature offers a convenient basis for the classification of thermotropic liquid crystals and is universally adopted.

Over the last twenty years thermotropic liquid crystals have found widespread applications. They are particularly useful as the materials in electrically controlled display devices, including watches, calculators, clocks etc. The most widely used materials for these purposes are based on nematic cyanobiphenyls (3). Other liquid crystalline systems with their electro-optical properties have been reported (51-53).

Recently thermotropic liquid crystals have been used in television screens and in instrumentation for vehicle dashboards, as well as in a variety of other display devices; chiral smectic C materials are becoming increasingly important here. Cholesteric liquid crystals find application in digital thermometers (54), biomedical thermography (55), thermal mapping (56), and decorative and novelty items (57,58).

Conventional liquid crystals have been low relative molecular mass systems which have found a wide range of applications (59). Their properties are well established and it has been shown that the molecular features responsible for mesomorphism are asymmetry of molecular shape and anisotropy of intermolecular forces. A recent development, however, has been the application of polymeric mesomorphic materials. The first of these were of biological origin, namely the tobacco mosaic virus (60) and a number of globular polymers (61). The first synthetic example was poly- -benzyl-L-glutamate (62,63). Since the early 1970s interest in these liquid crystal polymers has grown rapidly, mainly due to the advent of Kevlar by du Pont (64-66) and X-500 by Monsanto (67), both of which possess excellent mechanical properties.

Traditionally two major classes of liquid crystalline polymers have been identified and they can be obtained in two possible ways:

(1) by attaching the mesogenic groups to a polymer backbone thus giving side-chain liquid crystalline polymers;

(2) by introducing the mesogenic groups directly into a polymer backbone thus giving main chain liquid crystalline polymers.

More recently other variants have appeared; these are combined liquid crystalline polymers (68,69) which are hybrid between main chain and side-chain liquid crystalline polymers, and the rigid rod types described by Watanabe (70).

Such systems may be lyotropic or thermotropic and the subdivisions of mesogenic polymers are shown in Fig.9.

As previously mentioned, the molecular features responsible for liquid crystallinity are asymmetry of molecular shape and anisotropy of intermolecular forces. The former feature is dominant, especially among polymers (71,72). The latter feature, although of lesser importance in promoting liquid crystallinity, is usually responsible for the details of thermotropic behaviour (eg. transition temperature).

Nonamphiphilic monomer units are characterised by their rigid rodlike molecular structure. When the monomer units are joined to form the main chain, the polymer backbone becomes rigid and rodlike. The rodlike structure causes anisotropic packing of the macromolecules, as predicted theoretically by Flory (73). For mesogenic polymers, however, it is not necessary that the monomer units be rigid since chain rigidity can be caused by the secondary structure of the polymer. The liquid crystalline state can be observed for these mesogenic main chain polymers in solution as well as in the melt.

The nonamphiphilic mesogenic moiety can also be attached to the side chain. In contrast to the previously described mesogenic main chain polymers, in the liquid crystalline state only the original mesogenic side chains are responsible for the liquid crystalline order. This order is more or less independent of the conformation of the polymer main chain. The mesogenic side chain polymers consist of two components, the mesogenic moieties and the polymer main chain to which they are attached. A large number of known mesogenic molecules can be used as components and a variety of different polymer main chains are available. These mesogenic side chain polymers can be prepared by three different types of polymerisation (see Fig.10 for details). A lot of work on thermotropic side chain liquid crystals has been done by e.g. Ringsdorf, Percec and Finkelmann (74-76).

At the present time there have only been a few investigations in the field of polymeric lyotropic liquid crystalline systems. This thesis describes the synthesis and characterisation of novel polymeric, lyotropic liquid crystals. Following an introduction to surfactant chemistry (Chapter 2) the synthesis of the novel surfactants will be discussed in detail (Chapters 3 and 4). The majority of the work reported is concerned with the synthesis, as many experimental problems were encountered. However, having successfully isolated the desired, pure products, preliminary physical characterisations were undertaken and are reported in Chapter 6.

Fig.1 Schematic Representation of a Lamellar Phase.

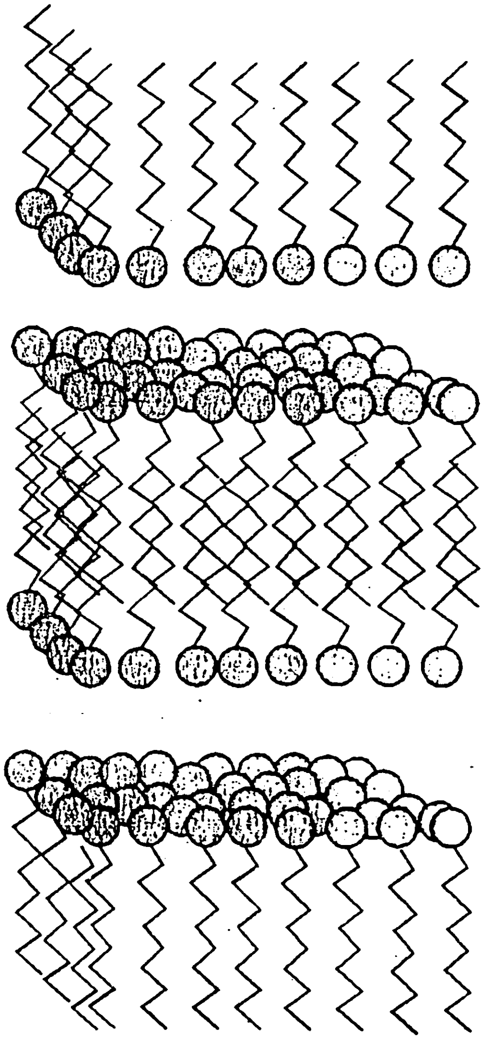


Fig.2 Schematic Representation of a Hexagonal Phase.

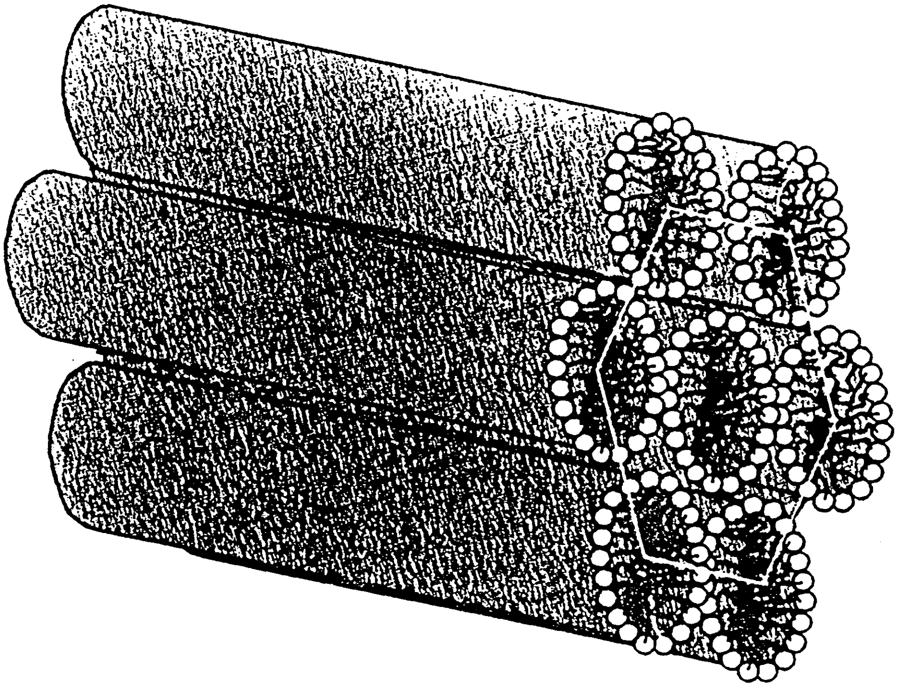


Fig.3 Schematic Represenation of an I_1 Body Centred Cubic.

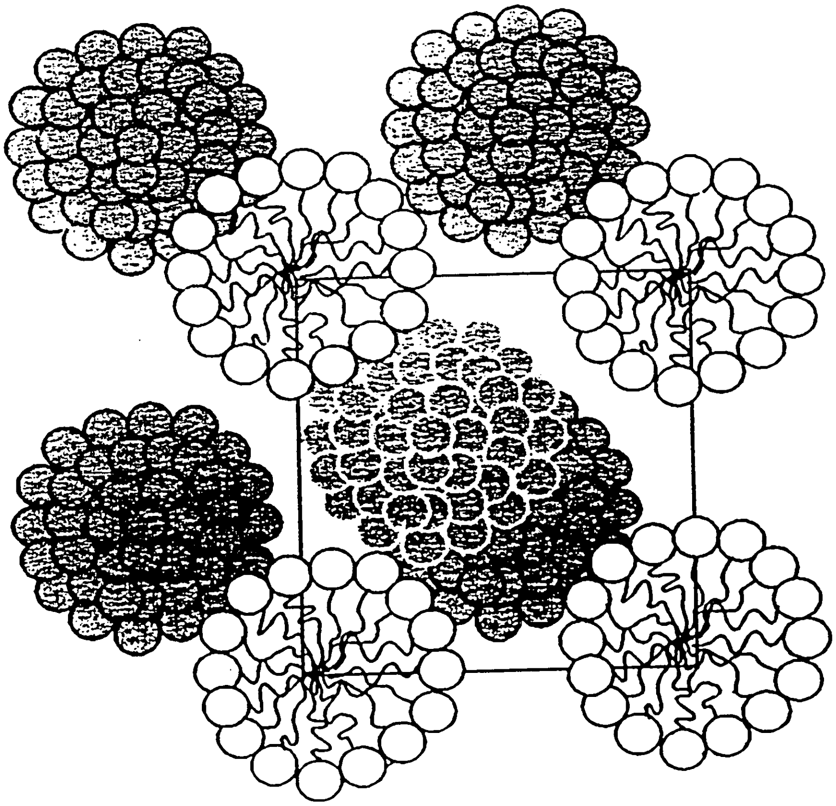
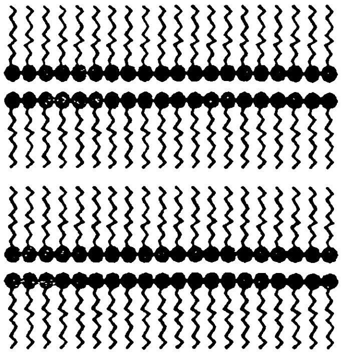
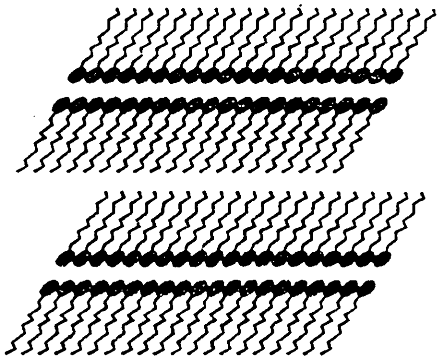


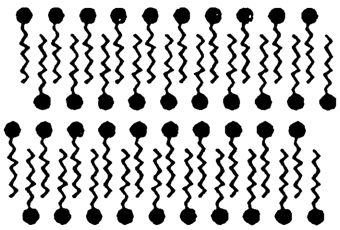
Fig.4 Three Common Gel Structures.



(a) Normal bilayer



(b) Tilted bilayer



(c) Interdigitated bilayer

Fig.5 Schematic Representation of a Nematic Phase (307).

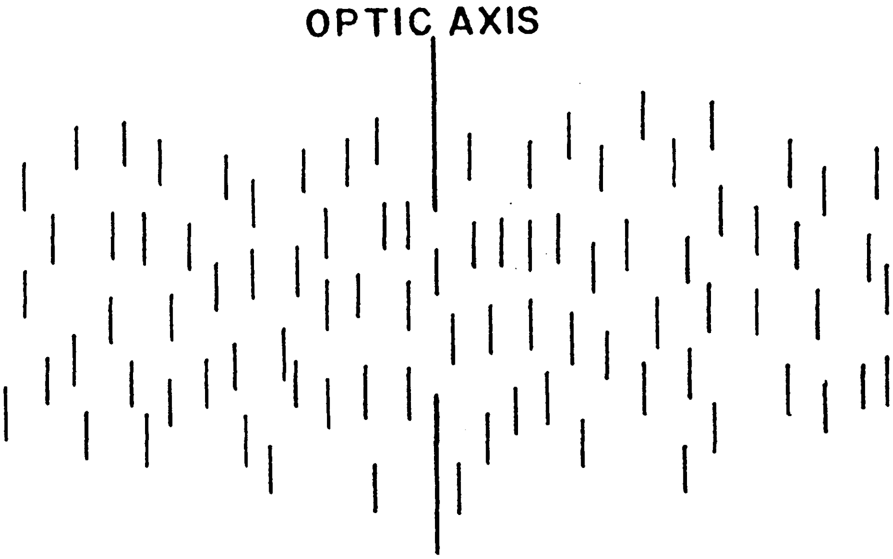


Fig.6 Schematic Representation of a Cholesteric Phase (307).

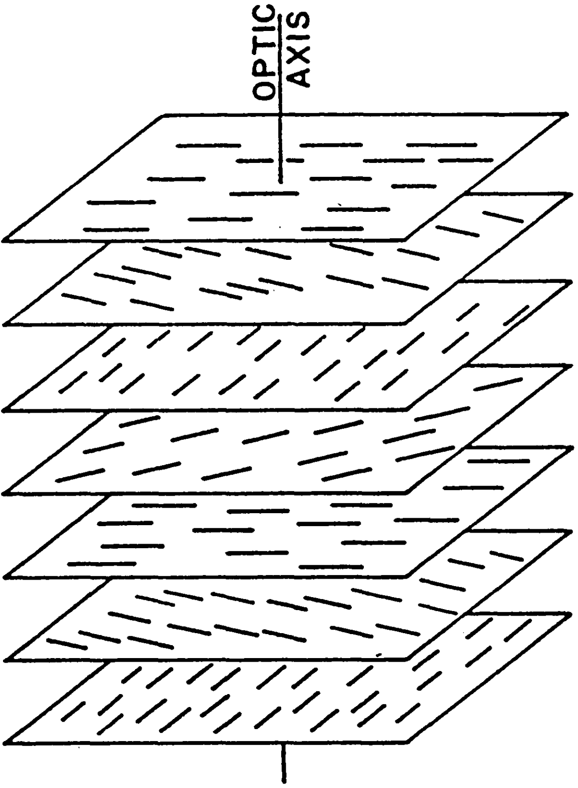


Fig.7 Schematic Representation of a Smectic A Phase (308).

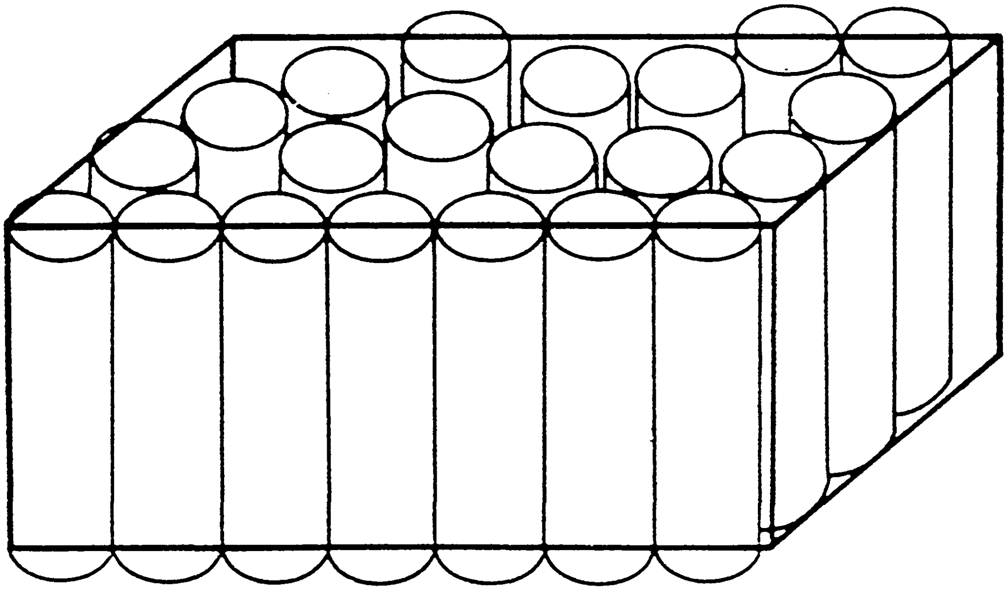


Fig.8 Schematic Representation of a Smectic C Phase (308).

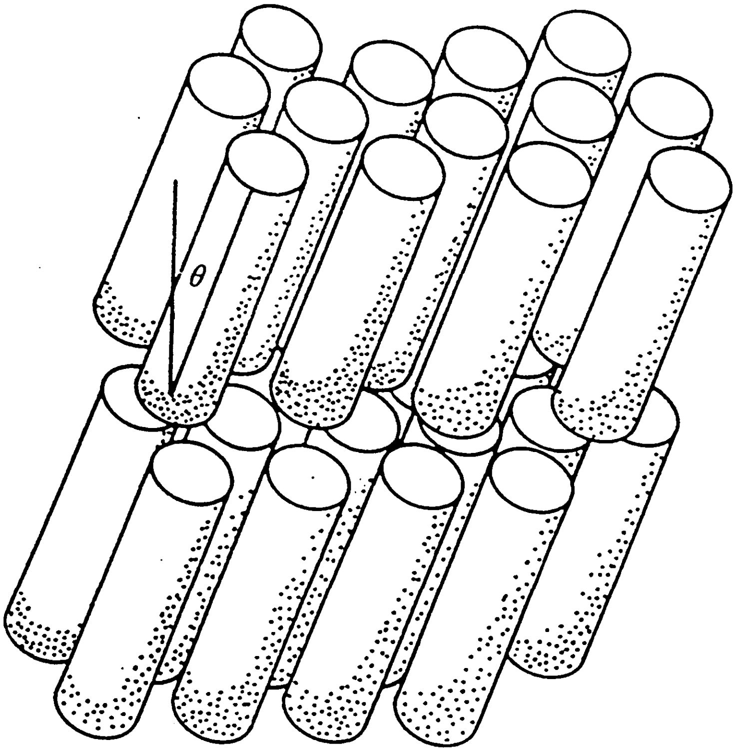


Fig.9 Classification of Liquid Crystalline Polymers (309).

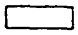
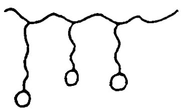
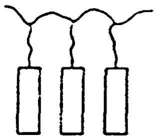
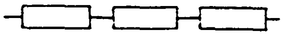
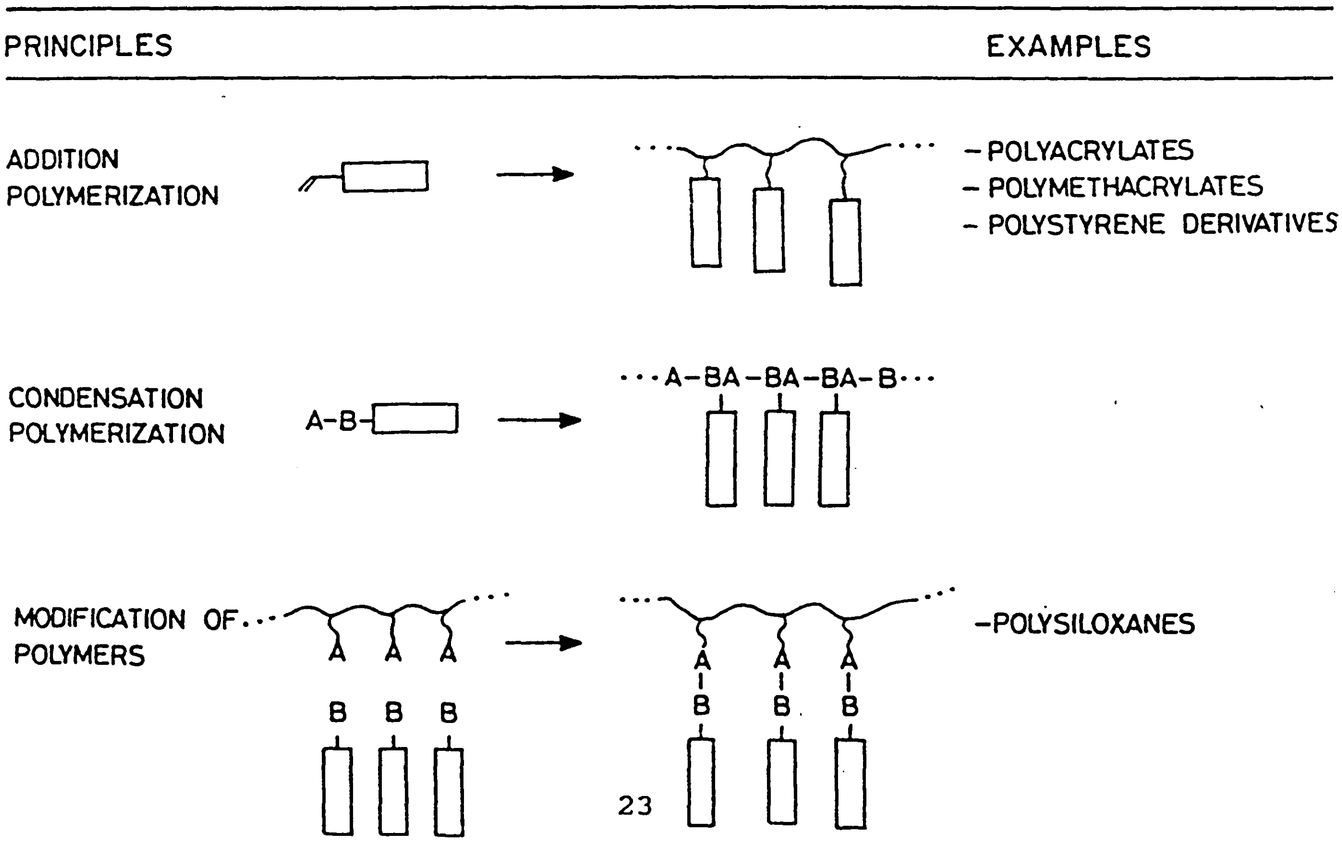
MONOMER UNIT	 AMPHIPHILIC		 NONAMPHIPHILIC	
POLYMER	 SIDE CHAIN	 MAIN CHAIN	 SIDE CHAIN	 MAIN CHAIN
PHASE BEHAVIOR	LYOTROPIC		THERMOTROPIC	THERMOTROPIC LYOTROPIC

Fig.10 Preparation of Mesogenic Side Chain Polymers (309).



2. Surfactants

2.1 Introduction

In simple terms a surfactant (or surface-active agent) can be defined as a soluble compound that reduces the surface tension of liquids, or reduces interfacial tension between two liquids or a liquid and a solid.

The earliest surfactants were soaps, such as the sodium salt of long chain fatty acids eg. $CH_3(CH_2)_nCOO^-Na^+$ (where n=14-18). These conventional materials comprise a polar head group and a hydrophobic, hydrocarbon chain (occasionally a fluorocarbon chain, which is also hydrophobic, is used); ie. they are amphiphilic (Fig.1). The hydrocarbon portion, which can be linear or branched, interacts only very weakly with the water molecules in an aqueous environment. Moreover, the strong interactions between the water molecules arising from dispersion forces and hydrogen bonding act cooperatively to squeeze the hydrocarbon out of the water, hence the chain is called hydrophobic. The polar or ionic portion of the molecule, usually termed the head-group, interacts strongly with the water via dipole-dipole or ion-dipole interactions and is solvated. Consequently the head-group is said to be hydrophilic.

The distinctive features of surface active agents are:

(1) their moderate maximum concentration of molecularly dispersed species;

(2) surface and interfacial tension depression in very dilute solution, due to the adsorption and orientation of molecules at the interface (see later);

(3) micelle formation above a certain concentration, which has been termed the critical micelle concentration (described later), due to the free energy decrease of the system;

(4) solubilisation of water-insoluble substances by micelles.

The balance between the hydrophobic and hydrophilic parts of the surfactant molecule gives rise to the special properties associated with surfactants.

Surfactants are classified depending on the nature of the head-group. Four basic classifications are known: anionic, cationic, nonionic and zwitterionic. Examples of each type are:

Anionic: sodium dodecanoate, $C_{11}H_{23}COO^-Na^+$

Cationic: hexadecyltrimethylammonium bromide, $C_{16}H_{33}N^+me_3Br^-$

Nonionic: hexaethyleneglycol mono n-dodecyl ether, $C_{12}H_{25}(OCH_2CH_2)_6OH$

Zwitterionic: 3-dimethyldodecylaminopropane sulphonate.

The unique property of these materials is their ability to adsorb strongly at various interfaces, for example, air-water, oil-water, water-solid, oil-solid etc. and to lower the interfacial surface energy, hence the term "surface active". Solubility of the material ensures that a reservoir of surface active agent is available to accommodate the large surface area of the various interfaces encountered in practical applications.

Surfactants are used in a number of fields which include detergents and other cleaning products (eg. soaps and shampoos), emulsifiers for foods, pesticides, cosmetics, oil recovery, drugs and medicines, wetting agents and many, many more.

2.2 Surfactant Solubility and The Krafft Temperature

Surfactants tend to concentrate at interfaces and thereby reduce the free energy of the system with which they interact. The primary mechanism for energy reduction in most cases will be adsorption at various interfaces, however, when all available interfaces are saturated, the overall energy reduction may continue through other mechanisms. The physical manifestation of one such mechanism is the crystallisation or precipitation of the solute from solution. An alternative is the formation of molecular aggregates or micelles that remain in "solution" as thermodynamically stable, dispersed species with properties distinct from those of the monomeric solution. While most common surfactants have a substantial solubility in water, that characteristic can vary significantly with changes in the length of the hydrophobic tail, the nature of the head group, the valency of the counterion, and the solution environment. For many ionic materials, for instance, it is found that the overall solubility of the material in water increases as the temperature increases. With ionic surfactants, it is often observed that the solubility of the material will undergo a sharp, discontinuous increase at a certain, characteristic temperature, known as the Krafft temperature (T_k). Below this temperature, the solubility of the surfactant is determined by the crystal lattice energy and heat of hydration of the system. The concentration of the monomeric species in solution will be limited to some equilibrium value determined by those properties. Above T_k, the solubility of the surfactant monomer increases to the point at which micelle formation begins and the aggregated species becomes the thermodynamically favoured form. The Krafft temperature can vary as a function of both the nature of the hydrophobic group and the character of the ionic interactions between the surfactant and its counterion. Nonionic surfactants, because of their different mechanism of solubilisation, do not exhibit a Krafft temperature.

2.3 Micelles and Critical Micelle Concentration

A surfactant optimises its environment by adsorption at an interface; a similar process can occur by self-association. When this happens it leads to ordered aggregates which are known as micelles. The aggregation of surfactant molecules to form micelles arises from the "hydrophobic effect" (77). Water-water hydrogen bonds are stronger than hydrocarbon water attractions, hence alkanes have a limited solubility in water. Polar molecules are soluble because of their strong solvation by water molecules. The polar head group of a surfactant increases the solubility of the monomer compared to that of the parent hydrocarbon. Aggregation of surfactant molecules reduces the contact of hydrocarbon chains with water, but allows the head groups to remain hydrated. Micelle formation, or micellisation, is an important phenomenon, not only because a number of important interfacial phenomena, such as detergency and solubilisation, depend on the existence of micelles in solution, but because it affects other interfacial phenomena, such as surface or interfacial tension reduction, that do not directly involve micelles.

It is noted that only polar solvents containing two or more potential hydrogen-bonding centres, thus capable of forming three-dimensional hydrogen-bonded networks, appear to lead to micelle formation (78). In non-polar solvents, clusters of surfactants may form, but they are generally not of colloidal size and their behaviour is not analogous to that of micelles in aqueous media. In some cases it is uncertain whether a particular surfactant aggregates to form micelles or to form lamellar liquid crystals (79,80). Surfactants that form micelles may also form liquid crystals at higher concentrations. Whether micelles or liquid-crystalline phases form in aqueous solution depends upon a number of structural properties, most importantly the number, length and branching of the hydrophobic chains (79), with increased length favouring liquid-crystal formation.

At very low surfactant concentrations in water there is insufficient association to form micelles, but at a particular concentration known as the critical micelle concentration (CMC) association is extensive. This sudden transition can be observed by plotting certain physical properties as a function of concentration, eg. osmotic pressure, solubilisation, surface tension, density, refractive index. The CMC is found at the point of the curve where a sharp change in gradient occurs (Fig.2). Above the CMC any further surfactant added does not significantly alter the monomer concentration. Instead there is an increase in the number of micelles formed. It is noted that as the micelles become bigger and more numerous a transition from a distorted state to an ordered array is produced, the micellar solution forms a lyotropic liquid crystalline phase (as described in Chapter 1).

There are a number of factors which affect the CMC and these will be discussed briefly below.

(1) <u>Surfactant Structure</u>

(a) The Hydrophobic Group:

In aqueous media, the CMC decreases as the number of carbon atoms in the hydrophobic group increases to about 16 and a generally used rule for ionic surfactants is that the CMC is halved by the addition of one methylene group to a straight-chain hydrophobic group attached to a single terminal hydrophilic group. For nonionics and zwitterionics the decrease with increase in the hydrophobic group is somewhat larger, an increase by two methylene units reducing the CMC to about one-tenth its previous value (compared to one-quarter in ionics). A phenyl group that is part of a hydrophobic group with a terminal hydrophilic group is equivalent to about three and one-half methylene groups. When the number of carbon atoms in a straight-chain hydrophobic group exceeds 16, however, the CMC no longer decreases so rapidly with increase in the length of the chain and when the chain exceeds 18 carbons it may remain substantially unchanged with further increase in the chain lengths (81). This may be due to the coiling of these long chains in water (82).

At this point it should be pointed out that a CMC is not observed in surfactants with hydrocarbon chains of less than seven carbon atoms.

Chain branching increases the CMC (83), as does the presence of double bonds in the hydrophobic chain (the cis isomer generally has a higher CMC than the trans isomer). Surfactants with either bulky hydrophobic or bulky hydrophilic groups have larger CMC values than those with similar, but less bulky, groups.

The substitution of polar groups into the chain, eg.-OH, generally causes a significant increase in the CMC, the carbon atoms between these polar groups and the hydrophilic group appearing to have about one-half of their usual effect on the CMC. However, when the polar group and the hydrophilic group are both attached to the same carbon atom, that carbon atom seems to have no effect on the value of the CMC.

The replacement of a hydrocarbon-based chain by a fluorocarbon-based one with the same number of carbon atoms appears to reduce the CMC. By contrast, the replacement of the terminal methyl group of a hydrocarbon-based hydrophobic group by a trifluoromethyl group has been shown to cause the CMC to increase.

(b) The Hydrophilic Group:

In aqueous media, ionic surfactants have much higher CMCs than nonionics containing equivalent hydrophobic groups. Zwitterionics appear to have smaller CMCs than ionics with the same number of carbon atoms in the hydrophobic chain.

If the hydrophilic group is moved from a terminal position to a more central position, the CMC increases. This is presumably due to the effective introduction of a branched chain (84).

The CMC is also increased when the charge on an ionic hydrophilic group is closer to the α-carbon atom of the (alkyl) hydrophobic group (85) and also when the surfactant contains more than one hydrophilic group in the molecule.

(c) The Counterion in Ionic Surfactants:

In anionic systems the nature of the counter ion does not greatly change the CMC, whereas in cationic systems a change from monovalent to divalent ion has a pronounced effect (86).

(2) <u>Electrolytes</u>

The presence of an electrolyte in aqueous solution causes a change in the CMC, the effect being more pronounced for anionic and cationic than for zwitterionic surfactants and more pronounced for zwitterionics than for nonionics. Experimental data indicate that for anionic and cationic surfactants, the effect of the concentration of electrolyte is given by (87):

$$\log \text{CMC} = - a \log C_i + b$$

where a and b = constants for a given ionic group at a temperature and C_i is the total counterion concentration in equivalents per litre.

The depression of the CMC in these cases is due mainly to the decrease in the thickness of the ionic atmosphere surrounding the ionic head groups in the presence of the additional electrolyte and the consequent decreased electrical repulsion between them in the micelle.

For nonionics and zwitterionics the above equation does not apply. The effect is given by (88-90):

$$\log \text{CMC} = -KC_s + \text{constant} \qquad (C_s < 1)$$

where K = constant for a particular surfactant, electrolyte and temperature;

and C_s = the concentration of electrolyte in moles per litre.

The change in the CMC of nonions and zwitterions on the addition of electrolyte has been attributed mainly to the "salting out" or "salting in" of the hydrophobic groups in the aqueous solvent by the electrolyte, rather than to the effect of the latter on the hydrophilic groups of the surfactant.

Mukerjee (91) and Ray (78,90) have suggested that the changes in CMC found for nonionic materials with electrolyte addition are related to the amount of work required to disrupt the structure of the aqueous solvent by the insertion of the surfactant molecule. If added electrolyte acts to enhance structure, that is, if it increases the organisation of the water molecules through the action of the added ions, the introduction of the monomeric surfactant molecule will require an additional amount of work to overcome that added structural energy. The net result will be a "salting out" of surfactant and a decrease in the CMC. If, on the other hand, the added electrolyte acts as a structure breaker, the required work will be less, the surfactant will be "salted in", and the CMC will increase.

The effectiveness of a given ion at altering the micellisation process can be qualitatively related to the radius of hydration of the added ions, with the contribution of the cations and anions being approximately additive. In general, the smaller the radius of hydration of the ion, the greater is its effect on the CMC. An order of effectiveness of anions at decreasing the CMC has been given by Ray (90).

(3) Added Organic Materials

It has been reported (92-94) that the effects of added organic materials on the CMC of ionic surfactants, while relatively small, can be experimentally significant, especially as the length of the hydrocarbon tail of the surfactant increases.

There are two classes of organic materials that change the critical micelle concentrations of aqueous solution surfactants. Class I materials change the CMC by being incorporated into the micelle, whereas Class II materials change the CMC by modifying solvent-micelle or solvent-surfactant interactions.

Materials in the first class, which reduce the CMC, are generally polar organic compounds, such as alcohols and amides. Shorter-chain members of the class are probably adsorbed mainly in the outer portion of the micelle close to the water-micelle "interface". The longer-chain members are probably adsorbed mainly in the outer portion of the core, between the surfactant molecules. Adsorption of the additives in these fashions decreases the work required for micellisation, in the case of ionic surfactants probably by decreasing the mutual repulsion of the ionic heads in the micelle.

Materials in the second class can either decrease or increase the CMC. The members of this class change the

CMC by modifying the interaction of water with the surfactant molecule or with the micelle. This may involve modifying the structure of the water, its dielectric constant, or its solubility parameter. Urea, formamide and guanidinium salts increase the CMC of surfactants in aqueous solution because of their disruption of the water structure (95). This may increase the degree of hydration of the hydrophilic group and, since hydration of the hydrophilic group opposes micellisation, cause an increase in the CMC. Materials that promote water structure, such as xylose and fructose, decrease the CMC (96).

(4) The Presence of a Second Liquid Phase

The CMC of the surfactant in the aqueous phase is changed very little by the presence of a second liquid phase in which the surfactant does not dissolve appreciably and which, in turn, either does not dissolve appreciably in the aqueous phase or is solubilised only in the inner core of the micelles. However, when the hydrocarbon is a short-chain unsaturated, or aromatic hydrocarbon, the value of the CMC is significantly less than that in air, with the more polar hydrocarbon causing a larger decrease (97-99). This is because some of the second liquid phase adsorbs in the outer portion of the surfactant micelle and acts as a Class I material.

On the other hand, the more polar ethyl acetate, as a second liquid phase, increases the CMC of sodium dodecyl sulphate slightly, either because it has appreciable solubility in water and thus increases its solubility parameter, or because the surfactant has appreciable solubility in the ethyl acetate phase, thus decreasing its concentration in the aqueous phase.

(5) Temperature

The effects of temperature on the CMC are complex. The value of the CMC decreases with temperature to a minimum and then increases with a further increase in temperature. The increase in the temperature has two main effects: it causes decreased hydration of the hydrophilic group, which favours micellisation, but it also causes disruption of the structured water surrounding the hydrophobic group, which disfavours micellisation. The relative magnitude of these two opposing effects, therefore, determines whether the CMC increases or decreases over a particular temperature range. Many papers have appeared in the literature detailing temperature effects on different surfactant systems (eg.100-102).

2.4 The Size and Shape of Micelles

The size, shape and charge of micelles have been studied mostly by light scattering (103-105), diffusion techniques, neutron scattering, osmosis (106) and viscosity measurements. Sedimentation data have also been used in conjunction with diffusion data, and micelle shapes ranging from the spherical through the cylindrical to the prolate ellipsoid have been deduced from the results (107,108).

McBain (109) reported that the osmotic activity of solutions of potassium stearate indicated the presence of a considerable degree of aggregation and suggested that the aggregated species should be termed micelles (described previously). To explain both the osmotic data and corresponding changes in conductance, McBain suggested the formation of two distinct types of micelle (as shown in Figs. 3 and 4). One is a spherical ionic micelle with not more than 10 like ions retaining their charges, formed in dilute solution before the critical micelle concentration; whereas the other is a micelle with little or no ionic charge, formed just beyond the critical micelle concentration so that the solution contains both highly conducting and practically nonconducting lamellar micelles. A lamellar micelle is described as comprising alternate layers of water and double amphiphilic molecules. These latter layers consist of the paraffin chains arranged parallel to each other, in liquid crystal rather than in crystalline packing. The depth of the layer is equal to the length of two fully extended paraffin chains placed end-to-end.

A far simpler model is that of Hartley (110,111). Up to the CMC, he considers that a paraffin chain salt is a strong electrolyte, completely dissociated and unaggregated. At the CMC, aggregation of the amphiphilic ion begins with the formation, at first, of relatively small micelles which grow rapidly over a limited concentration range to a size which for a given paraffin chain salt remains approximately constant with further increase in concentration (Fig.5). They are spherical or nearly spherical aggregates of about 50-100 surfactant molecules. The polar head groups are on the outside of the micelle in contact with the water, while the hydrophobic chains reside in the interior forming the core of the micelle. The core itself is believed to be liquid-like. The head-groups, because of their proximity, would require that some fraction be tightly bound to their counterions, thereby reducing repulsions between neighbours and reducing the overall mobility of the aggregated species in an electric field. The classical Hartley micelle successfully describes only a minority of surfactant systems.

The Hartley model is effective from many points of view although more recent work has indicated that rapid molecular motion causes the surface of the micelle to be somewhat 'rougher' than expected (112).

Harkins and Mittlemann (113) agree with Hartley's concept of one type of micelle, but from their x-ray results consider it to have some regularity of structure and picture it as disc-shaped or cylindrical. Their micelle is similar to the lamellar micelle proposed by McBain, but also resembles Hartley's micelle in respect to its conductivity.

Debye and Anacker (114) have interpreted the results of angular light scattering studies as indicating that neither a sphere nor a disc-shaped micelle is formed, but rather a rodlike micelle having the general shape of, say, a stack of coins (as shown in Fig.6). Such a model, derived from asymmetry studies, is not only in agreement with light scattering data but would also fit reasonably well into the kind of structure suggested by x-ray measurements of more concentrated solutions.

It is possible to predict the shape of micelles from packing constraints (115). To do this some basic assumptions must first be made: (1) The micelle interior contains only non-polar groups (ie. the head groups are in the water); (2) The micelle radius is smooth; (3) the maximum extension of the micelle radius is limited by the all trans chain length (L_t). The idealised micelle shapes are spheres, rods and bilayers. By comparing the shape and volume of a micelle to the shape and volume of a single surfactant molecule we can say mathematically:

$a = \frac{3V}{r}$ for spherical micelles;

$a = \frac{2V}{r}$ for rod micelles;

$a = \frac{V}{r}$ for bilayer micelles;

where a =area at micelle surface of a single surfactant molecule; r = radius of micelle; V = volume of single surfactant molecule.

Or, more practically:

$a > \frac{3V}{L_t}$ (spheres); $a > \frac{2V}{L_t}$ (rods); $a > \frac{V}{L_t}$ (bilayers)

So in conclusion, although the classical picture of a micelle is that of a sphere, most evidence suggests that spherical micelles are not the rule. Due to geometric packing requirements ellipsoidal, disk-shaped, and rod like structures may be the more commonly encountered micellar shapes. However, from the standpoint of providing a concept of micelles and micelle formation, the Hartley model remains a useful and meaningful tool.

2.5 Thermodynamics of Micellisation

While classical approaches based on phase separation and mass-action models have proven useful (see below), they do not possess the flexibility to extend their utility into areas such as the existence of cylindrical micelles, vesicles and bilayer structures. In attempting to devise a comprehensive theory for micelle formation, there are two possible approaches. One may begin with basic statistical mechanics, taking into account complex interactions between surfactant molecules and water, as well as solute-solute and solvent-solvent interactions. However, the fundamental principles of the hydrophobic interactions between small molecules in water are still not clearly defined. Alternatively one can ignore the statistical mechanical details in favour of an overall thermodynamic understanding. However, thermodynamics tend to be somewhat obscure and must eventually fall back upon some aspects of molecular interaction to validate the conclusions. It seems then, that a complete theoretical understanding of the surfactant aggregation process, that satisfies everyone, eludes us. However, the following discussion outlines the classical concepts of micelle formation.

In the literature on micelle formation two models have proved useful and have gained prominence: the mass action model, in which the micelles and monomeric species are considered to be in a chemical equilibrium, and the phase separation model, in which the micelles are considered to constitute a new phase formed in the system at and above the critical micelle concentration.

In the mass-action model it is assumed that an equilibrium exists between the monomeric surfactant and the micelles. For the case of nonionic surfactants the monomer/micelle equilibrium can be written:

$$nS \text{ (monomers)} \rightleftharpoons M \text{ (micelles)} \tag{2-1}$$

with a corresponding equilibrium constant, K_m, given by:

$$K_m = [M] / [S]^n \tag{2-2}$$

where brackets indicate concentrations and n is the number of monomers in the micelle, termed the aggregation number. In such a system the activity of the surfactant may increase with the total concentration above the CMC, although the increase may be very small. Equation 2-2 can be rewritten (as equation 2-2a) since the critical micelle concentration occurs at such low concentrations that activity coefficients can be assumed to be unity:

$$K_m = (cx/n) / [c(1-x)]^n \tag{2-2a}$$

where c denotes the concentration of surfactant in solution, x the fraction of monomer units in the aggregated state, and n the aggregation number.

The standard free energy of micelle formation per surfactant molecule is given by:

$$G_m = RT / n\ (n \ln [S] - \ln [M])$$

For an ionised surfactant, the presence of the counterion and its degree of association with the monomer and micelle must be taken into account. Therefore, the mass-action equation becomes:

$$nS^{-(+)} + (n-m)\ C^{+(-)} \rightleftharpoons M^{m(-or+)} \tag{2-1a}$$

where m is the concentration of free counterions, C. The degree of dissociation of the surfactant molecules in the micelle, a, or in effect the micellar charge, is given by a=m/n. The ionic equivalent of equation 2-2 is:

$$K_m = [M] / [S^{-(+)}]^{n} [C^{+(-)}]^{n-m} \quad (2\text{-}2b)$$

and the standard free energy of micelle formation at the CMC is given by:

$$\Delta G_m = RT (1+m/n) \ln CMC \quad (2\text{-}3)$$

In the phase separation model the micelle is assumed to be a separate but soluble phase which appears as the surfactant concentration reaches the CMC. The CMC, therefore, may be viewed as a solubility limit or saturation concentration for the monomeric species. This model gives the clearest definition of the CMC; however, it is now recognised that it only provides an approximate description.

For the surfactant molecule in water, the standard state is usually defined as the solvated monomer at unit mole fraction. In the micellar state of the phase separation model, the micelle is considered the standard state. If the chemical potential of the surfactant in solution and in the micelle are defined as u_s and u_m, respectively, then at equilibrium:

$$u_s = u_m \quad (2\text{-}4)$$

For a nonionic surfactant,

$$u_s = u_s^{\circ} + RT \ln a_s \quad (2\text{-}5)$$

where u_s° is the chemical potential in the standard state and a_s is the activity of the surfactant monomer. The free energy of micellisation can be given by:

$$\Delta G_m = RT\ (\ln CMC - \ln w) \qquad (2\text{-}6)$$

where w is the molar concentration of water (ie. 55.4 moles per litre at 20°C).

When ionisation of the surfactant molecule is involved, it is necessary to take into consideration the transfer of some portion of the counterions from the standard solution state to the micelle. The analogous equation, in concentration units, to equation 2-6 for ionic surfactants where no added electrolyte is present is:

$$\Delta G_m = (2-(p/n))\ RT\ (\ln CMC - \ln w) \quad (2\text{-}7)$$

where the bound fraction, p, is equal to (n-m).

In the presence of high neutral electrolyte concentrations, it is assumed that the micellar phase consists of the complete surfactant molecule, that is, an equivalent number of amphiphilic molecules and counterions, in which case equation 2-7 becomes:

$$\Delta G_m = 2RT\ (\ln CMC - \ln w) \qquad (2\text{-}8)$$

The most obvious criticism of the phase separation model is that it predicts that the activity of the monomeric surfactant species remains constant above the CMC. However, several surfactant systems have been found in which the activity of the monomer increases above the CMC.

Although the mass action model and the phase separation model are considered "classical" models, having been around for quite some time, they are by no means the only ones. For example, the multiple equilibrium model can be used to analyse the variation of the aggregation number of micelles with temperature and surfactant concentration (116). More recent approaches have presented more vigorous statements of the physical phenomena involved (117,118). An additional approach by Tanford (119), which was extended by Israelachvili (120), attempts to recognise the importance of molecular geometry in defining the characterisation of an aggregating system. Such an approach would seem to be especially useful for applications in which the chemical structure of the surfactant is of central importance.

2.6 Adsorption of Surface Active Agents at Interfaces

The forces responsible for micellisation also cause adsorption of surfactant molecules at interfaces. Wherever the aqueous solution meets a boundary surface the surfactant molecules can be orientated so that the tails are extruded from the water while the water-solubilising groups remain immersed in the water. Since location of a molecule in this position is energetically favoured, compared to the location of the molecule within the aqueous medium, the surfactant molecules will tend to accumulate in the surface in greater concentration than in the bulk solution. This greater surface concentration compared with bulk concentration is called adsorption. As the surface concentration builds up, the rate at which molecules return from the surface to the bulk by the ordinary process of diffusion will also increase, equilibrium being reached when the numbers of surfactant molecules entering and leaving the surface in a given time interval are equal.

Positive adsorption, the concentration of one component of a solution at a phase boundary, results in a lowering of the free surface energy of the solution. The quantitative relationship between the degree of adsorption at a solution interface and the lowering of the free surface energy, was deduced by Gibbs using complex thermodynamic methods (121,122); the surface excess of solute is proportional to the concentration of solute multiplied by the rate of change of surface tension, with respect to solute concentration. The concentration of a surfactant in a gas-liquid interface can be calculated from the linear segment of a plot of surface tension versus concentration and similarly for the concentration in a liquid-liquid interface from a plot of interfacial tension.

The adsorbed layer at gas-liquid or solid-liquid surfaces may have a complex composition in practical surfactant systems. The adsorbed molecules or ions may be close-packed forming almost a condensed film with solvent molecules virtually excluded from the surface, or they may be widely spaced and behave like a gas. The adsorbed layer can also be a multilayer rather than a monolayer (123).

The states of adsorbed layers have been studied by electron diffraction, x-ray diffraction, interferometry and electron microscope studies.

Fig.1 Surfactant Molecule

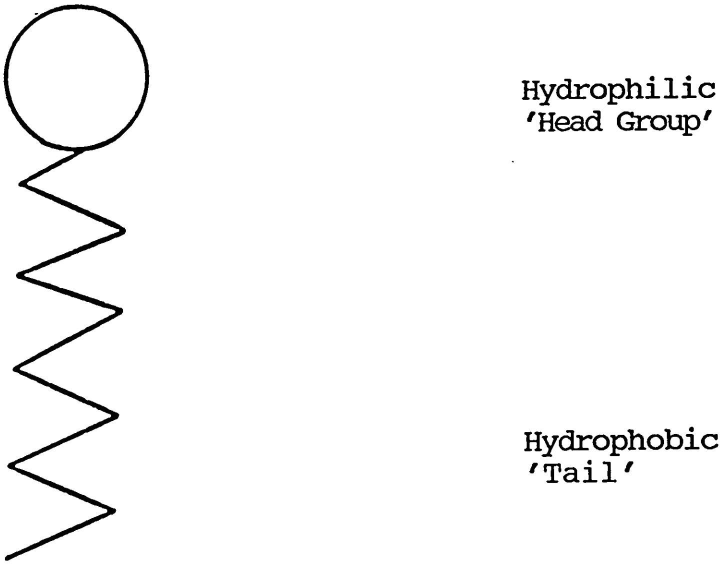


Fig.2 Concentration Dependences of Various Physico-Chemical Properties Around the Critical Micelle Concentration (310).

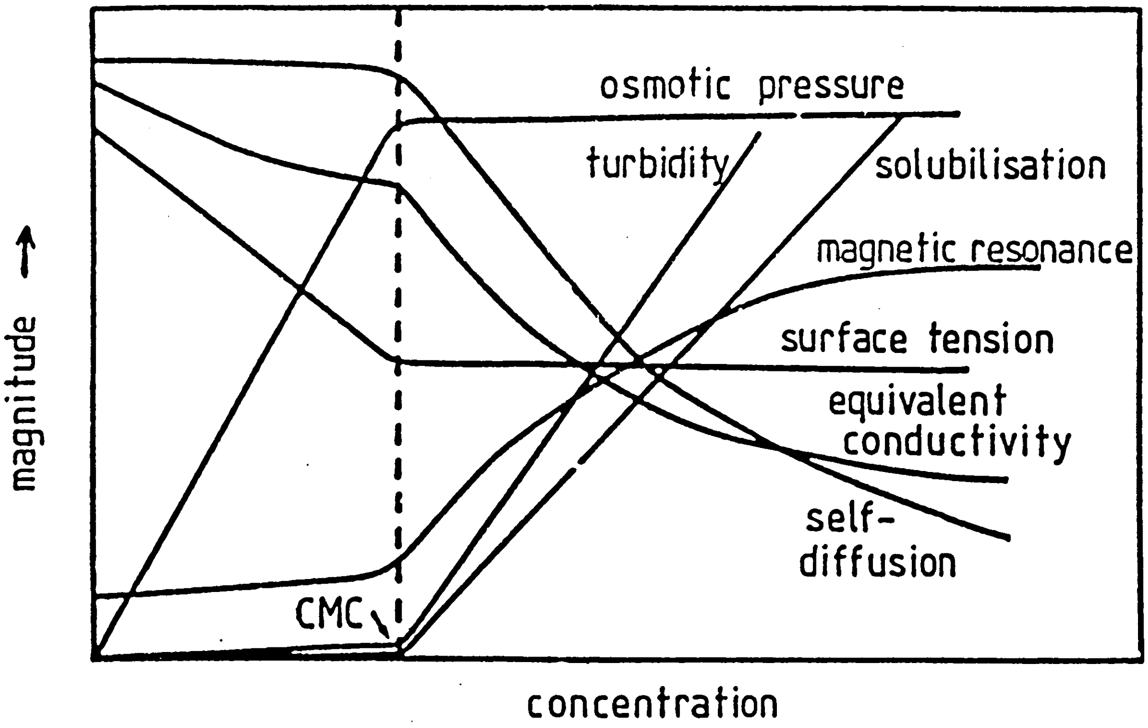


Fig.3 The McBain Spherical Ionic Micelle (311)

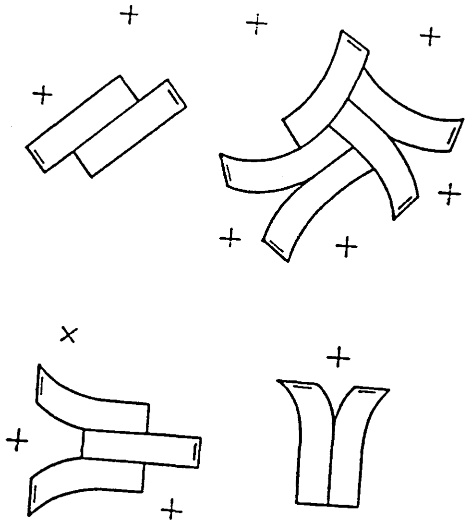


Fig. 4 The McBain Lamellar Micelle (311).

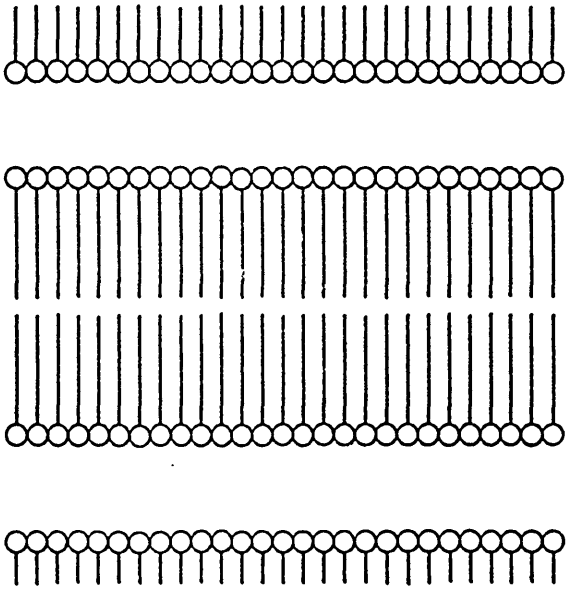


Fig.5 The Hartley Spherical Micelle

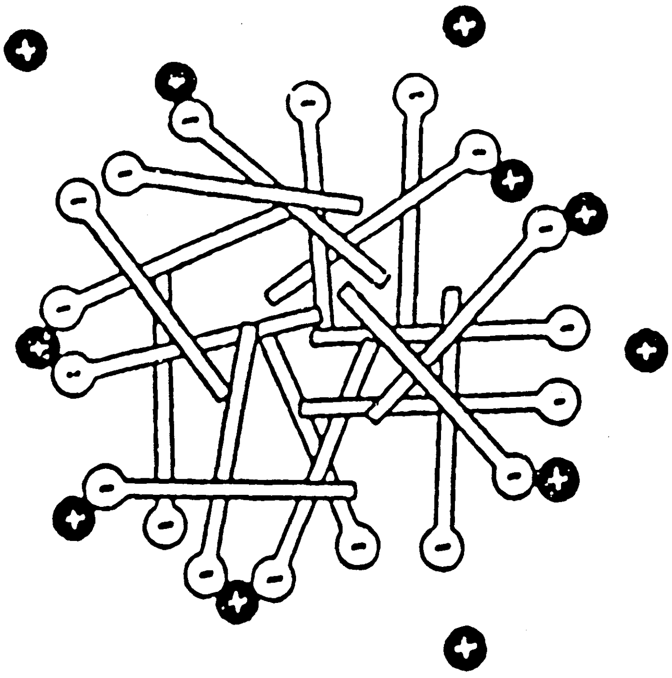
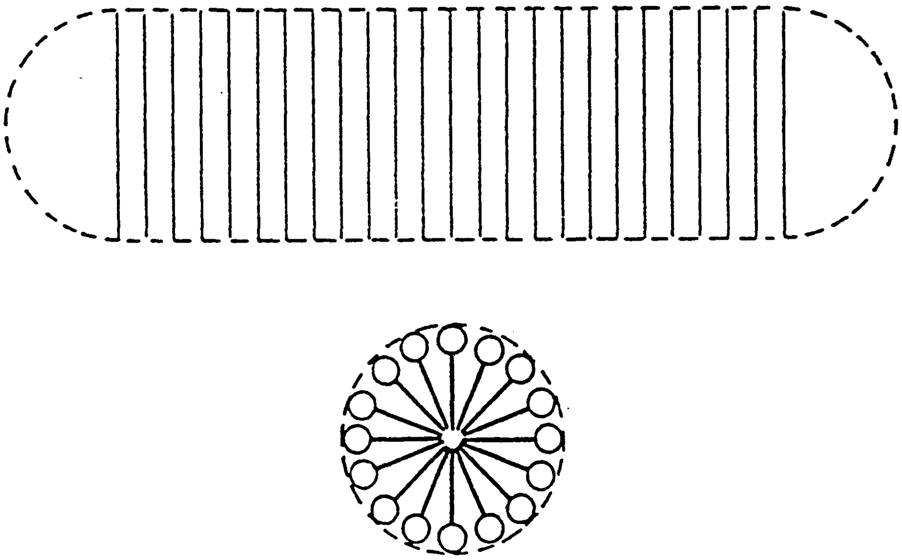


Fig.6 The Debye Rodlike Micelle (311).



3. The Synthesis of Novel Anionic Siloxane Surfactants

3.1 Introduction

As already discussed, conventional surfactant molecules comprise a polar head group and a hydrophobic, hydrocarbon chain. However, because long hydrocarbon chains have high melting points and low water solubility the length of the alkyl chain in these compounds is limited to ≤ ca C_{18} (longer-chain surfactants are usually insoluble). Therefore, in this project the alkyl group is replaced by a long, hydrophobic polydimethylsiloxane chain. Polydimethylsiloxanes are low melting compounds (glass transition at ca $^{-}120^{\circ}C$, melting transition at ca $^{-}35^{\circ}C$) with very flexible chains, and surfactants based on them might be readily soluble in water. Thus, it should be possible to synthesise liquid crystal polymers that undergo thermal transitions at low temperatures and have possible applications as thermotropic liquid crystals (124,125). The combination of the highly flexible, hydrophobic backbone also gives rise to possible interesting lyotropic behaviour (126). It is noted that, because of their extraordinary properties, silicone surfactants find applications in those areas where organic products are largely ineffective. This is primarily in organic media or in order to decrease the surface tension of aqueous systems to a greater degree than conventional surfactants (127-130).

This project has aimed to chemically attach amphiphilic mesogens to linear α - substituted siloxane backbones of varying lengths and then examine their surfactant properties. Therefore, the following type of structure was envisaged:

$m - (Si(CH_3)_2\ O)_n\ Si(CH_3)_2 - Bu$

where n = integer; Bu = Butyl group

m = amphiphilic mesogenic unit.

Sodium and calcium salts of a carboxylic acid were considered as appropriate polar head groups. One such compound has been previously synthesised (131) and is shown below:

$Bu - (Si(CH_3)_2\ O)_{12}\ Si(CH_3)_2\ (CH_2)_{10}\ COONa$

The above silicone surfactant contains a long alkyl portion, as well as the siloxane backbone, which could affect its surfactant properties. Therefore, one of the aims was to reduce the alkyl chain length to a minimum; the following surfactant was envisaged:

eg. $Bu - (Si(CH_3)_2\ O)_n\ Si(CH_3)_2\ (CH_2)_3\ COONa$

Also, it was thought that the use of a di-carboxyl head group, to increase the hydrophilic nature of the compound, would increase the head group activity and change the micelle size, shape and detergent properties.

Therefore, two classes of novel silicone surfactants were investigated:

(1) An α - substituted siloxane backbone with a mono-sodium or calcium salt of a carboxylic acid as the head group;

(2) An α - substituted siloxane backbone with a di-sodium or calcium salt of a dicarboxylic acid as the head group.

The synthesis of the desired product is basically a two step reaction; the silicone backbone is pre-formed and then linked to the appropriate organic molecule which carries the lyophilic function to produce the required finished product.

Polysiloxanes that have reactive functional groups such as SiCl, SiOR, or SiH are used as starting materials for the synthesis of organo-polysiloxane copolymers. These pre-polymers are gained either by hydrolysis of methylchlorosilanes or by the copolymerisation of cyclic or linear polymethylsiloxanes with functional siloxanes.

An equilibration reaction follows, whereby acid catalysts are used to cleave and relink the SiOSi bonds and thus bring the dimethylsiloxy and the functional siloxy groups into a statistical equilibrium. The equilibration reaction allows the production of reactive polysiloxanes with high reproducibility (132,133).

The reaction of these reactive siloxanes, with organic polymers or low molecular compounds containing functional groups, leads to organo-polysiloxane copolymers. A search of current literature shows that two types of reaction have become especially important:

(1) The esterification of chloropolysiloxanes with OH - functionalised organic compounds to give SiOC-linked copolymers.

(2) The hydrosilylating addition to unsaturated compounds (containing a C = C bond) of the Si-H function in the presence of platinum catalysts, whereby organo functional copolymers are formed, which are linked via Si-C bonds.

In most cases the Si-O-C link is hydrolytically much less stable than the Si-C link (132,134). For example, copolymers having SiOC links are cleaved hydrolytically in the presence of Lewis acids, organic acids or mineral acids, especially if they are soluble in water (however they are stable for the most part in neutral or amine-base environments). On the contrary SiC - bridged copolymers are stable in both amine-basic and slightly acid environments. It is for this reason that the hydrosilylation reaction was chosen to synthesise the desired products in our work.

The hydrosilylation reaction involves the addition to an alkene of an α Si-H functionalised siloxane in the presence of an appropriate catalyst.

eg. $Si - H + H_2 C = CHR \rightarrow Si - CH_2 CH_2 R$

It is also noted that among the main factors influencing the phase properties of a given polymer liquid crystal are:

(1) the purity,
(2) the average degree of polymerisation, and
(3) the polydispersity.

Therefore, by utilising the method of preforming the polymer backbone and then attaching the mesogen to it, it is possible to have greater control over these factors.

This chapter deals with all aspects of the synthesis of the desired novel surfactants and is divided into the following topics:

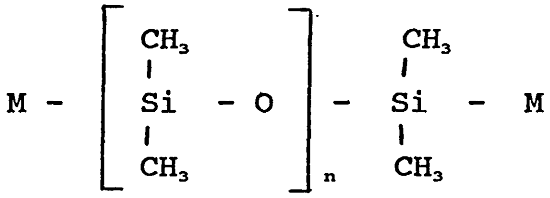
(1) the synthesis of the polydimethylsiloxane backbone,
(2) the hydrosilylation reaction, and
(3) the purification of the synthesised products.

3.2 The Synthesis of the Functionalised Siloxane.

Polysiloxanes are a group of materials having a silicon-oxygen backbone containing organic groups attached to the silicon atoms of the backbone. Commonly the organic groups are methyl and the polymers are called polydimethylsiloxanes.

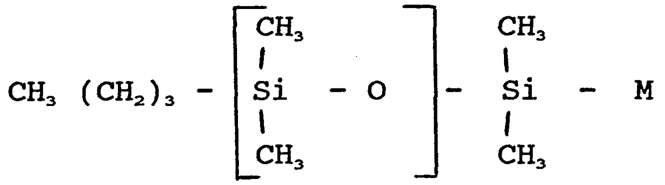
Silicone surfactants consist of a modified polydimethylsiloxane backbone in which one or more of the methyl groups is substituted by organic groups of hydrophilic or organophilic character; both frequently termed lyophilic. The silicone backbone itself behaves as the lyophobic part and can be considered to be a block of 'super-hydrocarbon' (135) because of the high concentration of methyl groups present. Its siloxane groups are present at the surface resulting in a poor compatibility with organic media (129). The structures of silicone surfactants are mainly of two types. One type bears its lyophilic groups at the end of siloxane chains, either as branched polyfunctional, linear difunctional (Fig.1) or linear monofunctional (Fig.2) systems. The second type is a rake or comb structure bearing modifications grafted onto the chain (Fig.3).

Fig.1 Difunctional linear type.



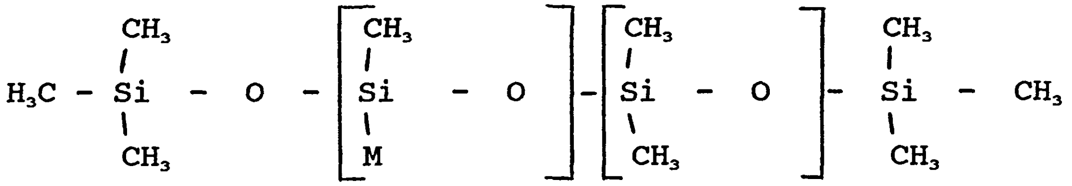
$$M-\left[\begin{array}{c}CH_3\\|\\Si\\|\\CH_3\end{array}-O\right]_n-\begin{array}{c}CH_3\\|\\Si\\|\\CH_3\end{array}-M$$

Fig.2 Monofunctional linear type.



$$CH_3(CH_2)_3-\left[\begin{array}{c}CH_3\\|\\Si\\|\\CH_3\end{array}-O\right]-\begin{array}{c}CH_3\\|\\Si\\|\\CH_3\end{array}-M$$

Fig. 3 Polyfunctional linear type.



$$H_3C-\begin{array}{c}CH_3\\|\\Si\\|\\CH_3\end{array}-O-\left[\begin{array}{c}CH_3\\|\\Si\\|\\M\end{array}-O\right]-\left[\begin{array}{c}CH_3\\|\\Si\\|\\CH_3\end{array}-O\right]-\begin{array}{c}CH_3\\|\\Si\\|\\CH_3\end{array}-CH_3$$

The letter M, in Figs. 1-3, represents either hydrophilic groups which can be anionic, cationic, amphoteric or non-ionic in character, or organophilic groups such as esters, amides and polyethers.

As previously stated, this project has been concerned with monofunctional linear polydimethylsiloxanes (Fig.2) and these alone will be discussed in detail.

Polydimethylsiloxanes are usually synthesised from chlorodimethylsilane. The process involves the hydrolysis of chlorodimethylsilane leading to a cyclic oligomer, and then polymerisation of this oligomer to give the desired product. Batch or continuous hydrolysis of chlorodimethylsilane can be used, but the continuous process is preferred (136). The reactions taking place during the hydrolysis include chlorosilane hydrolysis to silanols with rapid condensation of the silanols to form siloxanes:

$$SiCl + H_2O \rightarrow SiOH + HCl$$

$$SiOH + ClSi \rightarrow SiOSi + HCl$$

or

$$SiOH + HOSi \rightarrow SiOSi + H_2O$$

The hydrolysate is a mixture of roughly equal portions of linear, silanol-terminated, and cyclic polymers with the main component being the tetramer, ie. octamethylcyclotetrasiloxane:

$$(CH_3)_2\,SiCl_2 + H_2O \rightarrow HO[(CH_3)_2\,SiO]_nH + HCl \quad \text{Linear}$$

or

$$(CH_3)_2\,SiCl_2 + H_2O \rightarrow [(CH_3)_2\,SiO]_n + HCl \quad \text{Cyclic}$$

The hydrolysate can then be converted to cyclic compounds by thermal depolymerisation with base (137):

$$HO[(CH_3)_2\,SiO]_n\,H \xrightarrow[200^\circ C]{KOH} [(CH_3)_2\,SiO]_3 + [(CH_3)_2\,SiO]_4 \ldots + H_2O$$

As in the case with direct hydrolysis, the cyclic tetramer is the main component of the base-catalysed, thermal cracking process.

The α - Si - H functionalised siloxanes required are synthesised via the anionic polymerisation of hexamethylcyclotrisiloxane (D_3) (138) ie. the cyclic trimer. D_3 can be synthesised by the method outlined above but this type of reaction is difficult to control and the resulting mixture of products is difficult to resolve. Therefore, the D_3 was bought from a commercial source and used as supplied (139).

The structures of D_3 in the vapour phase and solid phase have been studied (140). The ring was found to be planar with methyl groups above and below the plane of the ring.

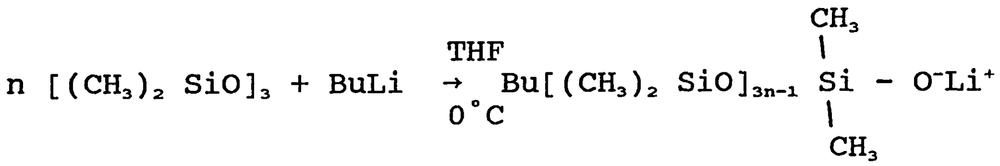
The anionic polymerisation of cyclosiloxanes has been studied extensively (eg. 138, 141, 142). Much of the published work refers to octamethylcyclotetrasiloxane (D_4) but the analogous polymerisation of D_3 will be discussed below.

Cyclosiloxanes readily undergo ring-opening polymerisation in the presence of a base or an acid catalyst to give high molecular weight polysiloxanes. The polymerisations can be carried out either in the bulk phase or in solution. Some base catalysts that have been employed include: alkali metal hydroxides, silanolates, alkoxides, potassium amide and sodium naphthalene. The acid catalysts which have been employed include mineral acids, Lewis acids, organic acids and acid clays. However, the base initiated polymerisation of D_3 with organolithium compounds, followed by end capping, is the preferred reaction. This type of polymerisation is termed a living polymerisation due to the absence of a termination step.

There is considerable steric strain associated with the cyclic trimer (which is absent in large ring and linear compounds) resulting in the greater reactivity of D_3 towards base. Hence, it is possible to selectively polymerise D_3 with the exclusion of the redistribution processes that occur in other equilibration reactions. Therefore, this anionic polymerisation gives linear polymers of narrow molecular weight distribution and free from cyclic material (141). The base initiator used is butyl lithium. If butyl lithium is mixed with D_3 in a hydrocarbon solvent $Bu - Si\ (CH_3)_2\ OLi$ is formed (143). No further polymerisation occurs even in the presence of excess D_3. However, when a donor solvent is added, a reasonably rapid polymerisation ensues producing an almost monodisperse polymer. It has been reported that some redistribution reactions do occur in such systems (144), but as they appear to be bimolecular in active centres they should be negligible under normal polymerisation conditions.

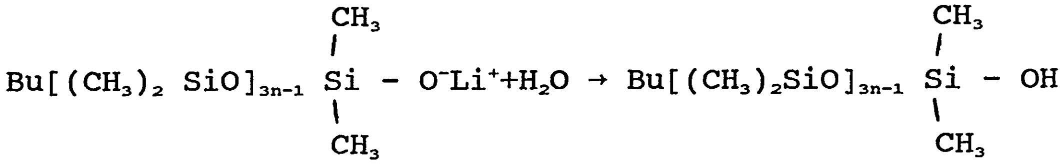
Accordingly, the polymerisation conditions adopted involved adding a solution of D_3 in tetrahydrofuran dropwise to a stirred solution of butyl lithium in hexane at 0°C (see Fig.4, and Chapter 4.1 for experimental details). The termination is achieved by the addition of water (Fig.5) to produce a silanol, which is then reacted with chlorodimethylsilane (Fig.6) to give the desired α - Si - H functionalised siloxane.

Fig.4 Anionic Polymerisation of D_3.



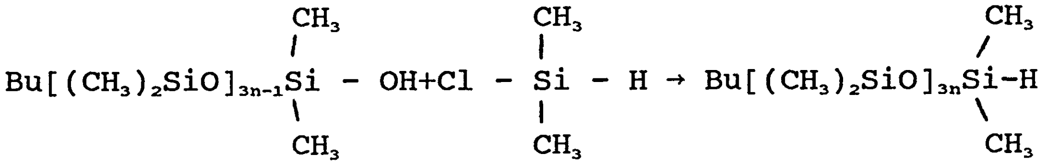
$$n\,[(CH_3)_2\,SiO]_3 + BuLi \xrightarrow[0^{\circ}C]{THF} Bu[(CH_3)_2\,SiO]_{3n-1}\,\overset{CH_3}{\underset{CH_3}{Si}} - O^-Li^+$$

Fig.5 The Termination Step.



$$Bu[(CH_3)_2\,SiO]_{3n-1}\,\overset{CH_3}{\underset{CH_3}{Si}} - O^-Li^+ + H_2O \rightarrow Bu[(CH_3)_2SiO]_{3n-1}\,\overset{CH_3}{\underset{CH_3}{Si}} - OH$$

Fig.6 Functionalisation Step.



$$Bu[(CH_3)_2SiO]_{3n-1}\overset{CH_3}{\underset{CH_3}{Si}} - OH + Cl - \overset{CH_3}{\underset{CH_3}{Si}} - H \rightarrow Bu[(CH_3)_2SiO]_{3n}\overset{CH_3}{\underset{CH_3}{Si}}-H$$

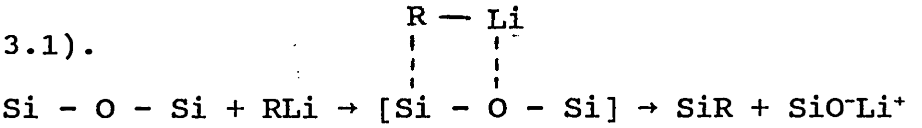
The RMM of the resulting siloxane is a function of the ratio of the amount of D_3 to the amount of initiator and is given by the following equation:

$$\bar{m}_n = \frac{D_3(g)}{nBuLi(m)} + 57 + 59 \qquad (145)$$

Where $\bar{m}_n$ = required number average molecular weight
57 = RMM of n Bu } Both included in the
59 = RMM of $(CH_3)_2$ SiH } siloxane structure.

The RMM of the siloxane was verified by ^1H nmr and GPC measurements.

The knowledge of the mechanism of this process is still limited (146). The mechanism is thought to proceed via a four membered cyclic transition complex (134) (Equation 3.1).



$$Si - O - Si + RLi \rightarrow [\overset{R\,-\,Li}{Si - O} - Si] \rightarrow SiR + SiO^-Li^+ \qquad (3.1)$$

3.3 The Hydrosilylation Reaction

The hydrosilylation reaction, applied to our aims, involves the addition of the α - SiH functionalised siloxane to an alkene containing the desired mesogenic group. This type of reaction emerged from the United States in the 1940s (147-151) and now constitutes an important method for the formation of the silicon-carbon bond, both from a synthetic and industrial viewpoint. Some major advantages of the hydrosilylation reaction, compared to other methods, include the possibility to introduce practically any functional group into the organosilicon compound, high product yields, simple equipment requirements and the opportunity to use a continuous process.

The hydrosilylation reaction may proceed thermally (152), by irradiation (148) or in the presence of a variety of catalysts. Many catalysts have been studied and these include:

(1) Peroxides, including dibenzoyl peroxide, t-butyl perbenzoate, t-butyl peracetate, di-t-butyl peroxide and methyl amyl ketone peroxide (153-155).

(2) metals and metal halides, including iridium, rhodium, platinum (used in an active form ie. as platinum black or precipitated on charcoal, silica gel or alumina), copper (156), nickel (157), titanium tetrachloride (158), tin, tin tetrachloride (159) and iron pentacarbonyl. However, the most

effective and widely used catalyst of this type is hexachloroplatinic acid ($H_2 Pt Cl_6 . 6H_2O$).

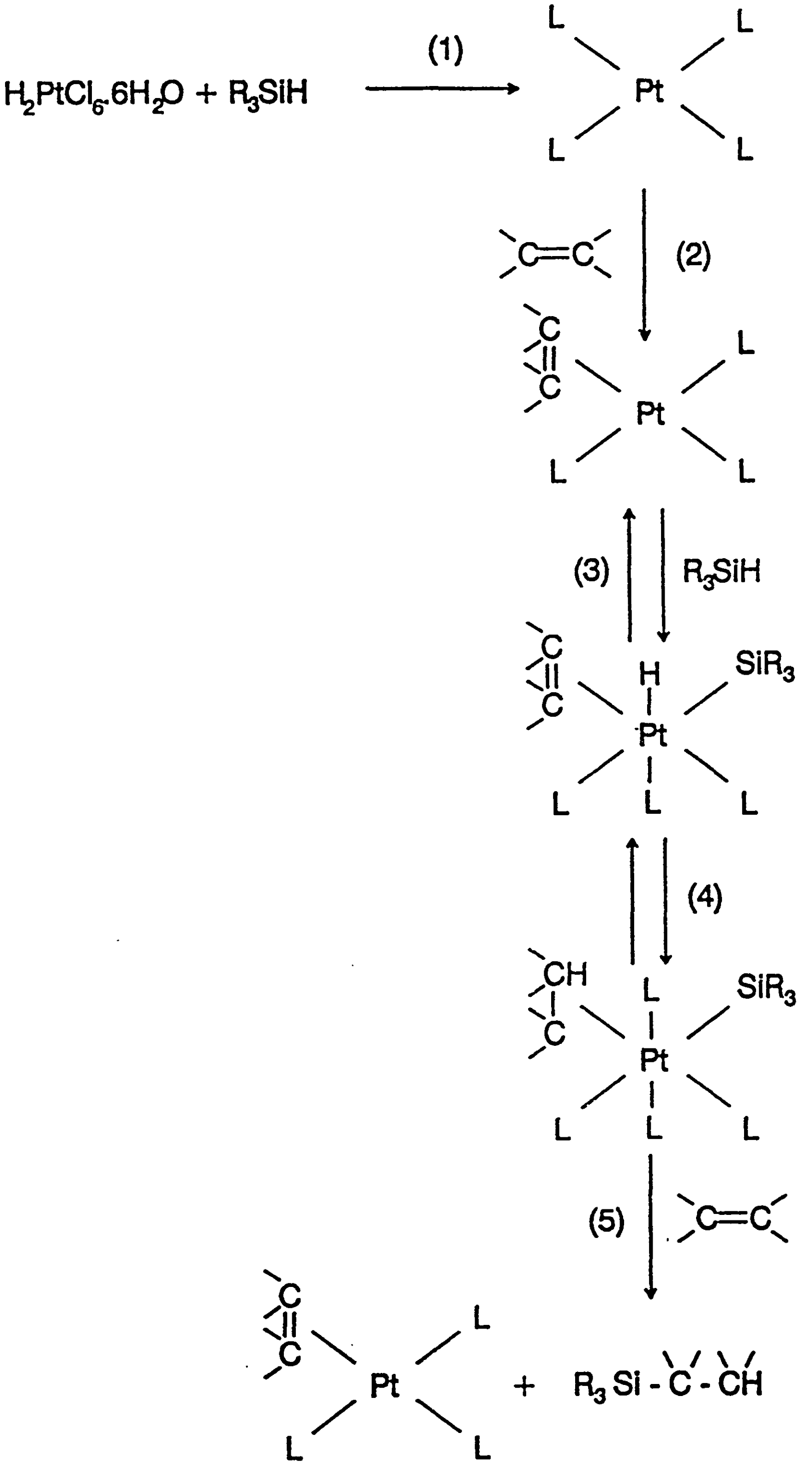
The use of hexachloroplatinic acid as a hydrosilylating catalyst is reported extensively (eg. 160-162) and in general, its solution in propan - 2 - ol is used. However, it has also been reported that solutions of hexachloroplatinic acid in various other solvents can be used; these solvents include tetrahydrofuran (163,164), methanol (165), ethanol (166), butanol (167), octanol (168,169), and cyclohexanone (170).

Hexachloroplatinic acid has the advantages of being effective at very low concentrations (10^{-5} M or even less in certain cases), the avoidance of excessive heat to carry out the reaction, the ability to carry out the reaction in the absence of solvent (if required), and it is also very tolerant of a range of organic functionality, including nitro, cyano, ester and phosphine oxides, among others. For these reasons, hexachloroplatinic acid was the chosen catalyst in all the hydrosilylation reactions carried out during this study.

It is widely accepted that the hydrosilylation reaction, using hexachloroplatinic acid as catalyst, proceeds via a coordination mechanism (171-175) and the scheme outlined in Fig.7 has been proposed (172,173,176). The initial reaction (step 1) involves the siloxane reduction of the catalyst, a d^6Pt (IV) complex. The resulting square-planar d^8Pt (II) complex then (step 2) co-ordinates, and hence activates, the substrate alkene. The co-ordinated alkene is known to show enhanced susceptibility to attack by nucleophiles. In step 3, the siloxane adds oxidatively, to provide a d^6 octahedral intermediate. Step 4 is thought to be the rate-determining step and involves a rearrangement from an alkene π - complex to an alkyl σ - complex. The latter reacts with more alkene (step 5), regenerating the product from step 2 and forming the hydrosilylated product. Lukevics (177) listed the factors confirming these mechanistic steps (175, 178-182).

Fig.7 Hydrosilylation Mechanism for Hexachloroplatinic Acid.

L = unspecified ligand, presumably chlorine, hydrogen, or coordinated solvent.



The above mechanism applies to the hydrosilylation reaction when using freshly prepared solutions of hexachloroplatinic acid in propan - 2 - ol. However, Pucknarevich (183) noted that the Pt (IV) was gradually reduced to Pt (II) (and Pt (0)) with the simultaneous formation of propanone:

$H_2PtCl_6.6H_2O + (CH_3)_2\ CHOH \rightarrow H_2\ PtCl_4 + (CH_3)_2\ CO + 2HCl + 6H_2O$

Whilst both Pt (II) and Pt (0) catalyse the desired hydrosilylation reaction they also catalyse undesirable side reactions (184,185):

(1) $2\ \text{-(Si-H)} + Pt(II) + [O] \rightarrow \text{- Si-O-Si-} + Pt(0) + H_2 \uparrow$

(2) Pt catalysed reactions leading to splitting of Si-C bonds.

Gray (186) noted that products formed from hydrosilylations using older (>4 weeks) catalyst solutions were discoloured compared to the cream/white products resulting from those hydrosilylations using freshly prepared catalyst solutions. He also noted that the products had different phase properties. The reason for these differences can be explained in terms of the above side reactions, eg. finely divided Pt (0) is thought to cause the discolouration of the product. It is for these reasons that only freshly prepared catalyst solutions were used in all the hydrosilylation reactions carried out.

As well as using fresh catalyst solutions, moisture and light must be rigorously excluded from the reactions.

Also, all mesogenic precursors have to be removed from the product liquid crystal polymers as low RMM liquid crystal materials have a large effect on the properties of the liquid crystal polymers. Isolation of the products can be achieved by gel permeation chromatography (187), precipitation (188-191) and, where the products are volatile, distillation. In general precipitation is the preferred method of isolation and has been used throughout this study.

The target compound was a siloxane backbone with a head group containing one or two carboxyl functionalities. Therefore, the ideal mesogen, for the hydrosilylation reaction, was considered to be a mono- or di- carboxylic acid containing an alkene functionality. The following carboxylic acids were thus considered as possible mesogens: vinylacetic acid ($CH_2 = CH\ CH_2\ COOH$), allylmalonic acid ($CH_2 = CH\ CH_2\ CH\ (COOH)_2$), itaconic acid, fumaric acid (trans - $HO_2\ CCH = CH\ CO_2\ H$) and maleic acid (cis - $HO_2\ CCH = CHCO_2H$). One consideration however, was that hexachloroplatinic acid also catalyses the reaction of a silyl group with a free carboxylic acid:

eg. $Si - H + CH_2 = CHCOOH \rightarrow CH_2 = CHCOOSi + H_2\uparrow$

Hence, it is necessary to protect the carboxylic acid groups prior to hydrosilylation. An appropriate protecting group had to be found whose attachment could be achieved without the use of a strong acid catalyst (which might attack the terminal vinyl group of the amphiphile). Also the subsequent removal of the protecting group must be quantitative and carried out without the use of strong acids or bases, as these may lead to the breakdown of the siloxane backbone.

The ultimate products required were the sodium or calcium salts of the acids, attached to the polydimethylsiloxane backbone. Therefore, the ideal mesogens would be salts of the mono-olefinic carboxylic acids listed above. The preparation of the sodium salts of acids is a simple process in which the acid is neutralised by sodium ethoxide in ethanol:

eg. $CH_2 = CHCH_2CO_2H + C_2H_5ONa \rightarrow CH_2 = CHCH_2CO_2Na + C_2H_5OH$

The precipitated salt is filtered and dried to a constant weight at 110°C. For the successful attachment of this compound to the α - SiH - functionalised siloxane a common solvent, for both the salt and the siloxane polymer, had to be found. However, no common solvent was available.

For the preparation of the calcium salts of the acids, the acid is reacted with ammonium hydroxide in ethanol and then with calcium chloride to produce the solid salt. The precipitated salt is then filtered and dried to a constant weight.

eg. $CH_2 = CHCH_2CO_2H + NH_4OH \rightarrow CH_2 = CHCH_2CO_2NH_4 + H_2O$

then

$$2CH_2 = CHCH_2CO_2NH_4 + CaCl_2 \rightarrow (CH_2 = CHCH_2CO_2^-)_2Ca^{2+} + 2NH_4Cl$$

However, once again, no common solvent, for both the salt and siloxane polymer, was found. Therefore, the formation of the salt must be performed after the hydrosilylation reaction and so an alternative protecting group, which meets the constraints listed above, had to be found.

A wide variety of protecting groups for carboxylic acids are known (192,193) including many organosilicon groups (194), for example: trimethylsilyl esters, triethylsilyl esters (195), t-butyldimethylsilyl esters (196-198), i-propyldimethylsilyl esters (199,200), phenyldimethylsilyl esters (201) and trimethylsilylethyl esters (202). However, the simplest and most convenient protecting groups, as they are commercially available, are the methyl or ethyl esters of the aforementioned mono/di carboxylic acids. Unfortunately deprotection is usually achieved using strong bases or acids which may ultimately break up the siloxane backbone. This apart, these esters were considered the ideal mesogens for preliminary studies of the hydrosilylation reactions required.

3.3.1 The Hydrosilylation of Methyl and Ethyl Esters.

Hydrosilylation reactions were carried out on the following esters: methyl acrylate ($CH_2 = CHCOOCH_3$), methyl vinylacetate ($CH_2 = CHCH_2CO_2CH_3$), diethyl allylmalonate ($CH_2 = CHCH_2CH(CO_2C_2H_5)_2$), dimethyl itaconate, diethyl fumarate (trans - $H_5C_2O_2CCH = CHCO_2C_2H_5$) and diethyl maleate (cis - $H_5C_2O_2CCH = CHCO_2C_2H_5$):

eg.

$$\mathrm{Bu{-}(Si(CH_3)_2O)_nSi(CH_3)_2H + CH_2 = CHCOOCH_3 \rightarrow Bu{-}(Si(CH_3)_2O)_nSi(CH_3)_2(CH_2)_2\,COOCH_3}$$

All the hydrosilylations attempted were successful under the conditions outlined in Chapter 4.2. Deprotection of the hydrosilylated products, to yield the desired acid compounds, proved to be, as feared, very difficult. The main problem was that the harsh conditions required for de-esterification, broke up the siloxane backbone.

To examine the feasibility of various reactions, preliminary de-esterifications were attempted on diethyl allylmalonate as it is cheap and the product (ie. allylmalonic acid) has a known melting point and IR and ^1H nmr spectra.

Ester hydrolysis is usually catalysed by acids or bases. When bases catalyse the reaction, the attacking species is the powerful OH^- nucleophile. This reaction is called saponification and gives the salt of the acid:

eg. $$\mathrm{CH_2 = CHCH_2\,CH(CO_2C_2H_5)_2 \xrightarrow[H_2O]{2OH^-} CH_2 = CHCH_2\,CH(CO_2^-)_2 + 2C_2H_5OH}$$

The hydrolysis of diethyl allylmalonate using potassium hydroxide proved highly effective (see Chapter 4.3.1 for experimental details). However, when this reaction was attempted on a hydrosilylated product the strong base, coupled with the high temperature, broke up the siloxane backbone. Therefore, as expected, this method proved unsuitable for the deprotections.

The same reaction components were again employed, but instead of refluxing for two and a half hours, the reaction mixture was stirred at room temperature for seven days. Again, the diethyl allylmalonate was successfully converted to the diacid, but when trying to de-esterify the hydrosilylated product, the siloxane backbone was broken up.

The above ester hydrolysis was then tried with sodium hydroxide and although diethyl allylmalonate was successfully converted to the diacid, once again, the Si-O bonds were broken when the de-esterification of the hydrosilylated product was attempted.

It was noted that, during the above hydrolysis reactions, reaction mixtures were not homogenous throughout ie. two distinct layers were noted. By keeping the reaction mixture homogenous, at all times, it was hoped to hydrolise the esters without damaging the siloxane backbone (see Chapter 4.3.2 for experimental details). However, it was found that the siloxane backbone was broken up under these conditions. Therefore, it was concluded that a strong base could not be used to deprotect the hydrosilylated products as the Si-O bonds of the siloxane backbone were broken.

Several procedures for the hydrolysis of alkyl carboxylic esters have been developed which allow for hydrolysis under neutral conditions (203-206). However, these procedures usually require the use of strong nucleophiles and high temperatures to effect dealkylation and this would lead to the destruction of the siloxane backbone. It has been reported (207-212), however, that iodotrimethylsilane was found to be an extremely efficient reagent for the dealkylation of esters under strictly neutral and very mild reaction conditions to yield the corresponding silyl esters which were hydrolysed upon aqueous work up to the carboxylic acids.
eg. $RCO_2R^1 \rightarrow RCO_2Si(CH_3)_3 \rightarrow RCO_2H$

Because of the difficulties associated with handling iodotrimethylsilane a great deal of attention has been focused on the dealkylation of esters with iodotrimethylsilane generated in situ from eg. chlorotrimethylsilane/sodium iodide in acetonitrile (207,208). The following mechanism has been proposed (213):

$$CH_3CN + (CH_3)_3SiCl + NaI \rightarrow [CH_3CN^+Si(CH_3)_3]\ I^- + NaCl$$

This in situ method was attempted (see Chapter 4.3.3 for experimental details) but it proved unsuccessful in the conversion of diethyl allylmalonate to allylmalonic acid. The de-esterification reaction was then attempted using commercially available (139) iodotrimethylsilane but, once again, this was unsuccessful.

Therefore, the use of an alternative protecting group was considered to be the most likely route to the desired products. As previously mentioned, many organosilicon groups can be used for the protection of carboxylic acids. One such protecting group is a silyl ester, which can be easily removed without the use of acids or bases and under mild reaction conditions. The simplest silyl ester is trimethylsilyl which can be removed with water (or alcohols).

3.3.2 The Hydrosilylation of Silyl Esters.

A search of the literature indicated that there were three main methods for the protection of carboxylic acids using the trimethylsilyl group:

(1) Using trimethylchlorosilane;
(2) Using N-trimethylsilylacetamide (214);
(3) Using ketene methyl trialkylsilyl acetals (215).

The major disadvantages of methods (1) and (2) over method (3) were considered to be:

(a) Strong base, acid or catalyst is required.
(b) A large amount of by-product such as inorganic salt or HCl-amine salt is produced with the moisture sensitive silyl esters.
(c) Product yields are not always high.

However, the method using trimethylchlorosilane (see Chapter 4.4 for experimental details and Fig.8) was ultimately chosen, as the synthesis was easy and quick to perform, the reagents are cheap, yields were found to be high and the HCl-amine salt by-product was easily removed by filtration.

All the dicarboxylic acids previously mentioned were successfully disilyl protected and Table 1 shows the properties of the resulting products. It is noted that the disilyl protected mesogens are air/moisture sensitive and therefore should be stored under nitrogen.

Fig.8 Disilyl Protection (Py = pyridine)

eg.

$$CH_2 = CHCH_2CH(CO_2H)_2 + 2(CH_3)_3SiCl \rightleftharpoons CH_2 = CHCH_2CH(CO_2Si(CH_3)_3)_2 + 2HCl$$

$$2HCl + 2\,Py \rightarrow 2\,Py\,HCl$$

The silyl protecting group is known to be particularly labile and the method of hydrosilylation, whereby the catalyst is dissolved in a small amount of propan-2-ol, cannot be used as the alcohol leads to the deprotection of the acid. Therefore, alternative hydrosilylation conditions were investigated. Hexachloroplatinic acid is insoluble in toluene, therefore, dry tetrahydrofuran was used and the method employed is detailed in Chapter 4.5. Hydrosilylations of all four disilyl protected acids were attempted but all proved unsuccessful.

Initially it was thought the hydrosilylation method used might be unsuitable. However, a hydrosilylation of diethyl allylmalonate, using this method, proved successful.

The purities of the disilyl protected acids were then investigated. Impurities in a protected acid could poison the catalyst resulting in the failure of the hydrosilylation. A commercially available silyl protected acid, namely trimethylsilyl methacrylate (139), with a reported purity of greater than 98%, was obtained and a hydrosilylation attempted. This silyl protected acid is analogous to methyl acrylate (which has been successfully hydrosilylated) ie. they both contain one "carboxylic acid group" adjacent to the double bond. Hydrosilylation of the commercial trimethylsilyl methacrylate proved unsuccessful and it was therefore concluded that other factors must be contributing to the failure of the hydrosilylation reactions.

TABLE 1. DISILYL PROTECTED MESOGENS

Product	Boiling Point	Appearance	% Yield	Melting Point /°C
Disilyl Fumarate	1) 94°C/2.33mmHg 2) 250°C/760mmHg	White Solid	71	60-62
Disilyl Itaconate	1) 66°C/0.4mmHg 2) 250°C/760mmHg	Colourless Liquid	69	-
Disilyl Allylmalonate	1) 91°C/1.5mmHg 2) 310°C/760mmHg	Colourless Liquid	67	-
Disilyl Maleate	1) 70°C/3.5mmHg 2) 210°C/760mmHg	White Solid	70	-

One difference between the diesters and the disilyl protected acids is the relative size of the protecting groups; the silyl group is far bulkier. It has been reported (216) that the hydrosilylation reaction is greatly influenced by steric considerations and therefore steric hindrance, due to the bulky nature of the trimethylsilyl groups, could be the cause of the unsuccessful hydrosilylations.

It is noted that Cockett (131) has successfully hydrosilylated the trimethylsilyl ester of 10-undecenoic acid ($CH_2 = CH(CH_2)_8\ CO_2Si(CH_3)_3$). This reaction was verified here and therefore, it can be concluded that the close proximity of the protected acid groups to the double bond is the most likely reason for the unsuccessful hydrosilylations detailed above. It was thought that by increasing the number of $- CH_2 -$ groups between the dicarboxyl functionality and the double bond a successful hydrosilylation of a diacid could be achieved. The following two mesogens were therefore synthesised:

(1) $CH_2 = CH(CH_2)_2\ CH(CO_2H)_2$ synthesised from 4-bromo-1-butene.

(2) $CH_2 = CH(CH_2)_3\ CH(CO_2H)_2$ synthesised from 5-bromo-1-pentene.

Fig.9 shows the reaction scheme employed. It proved highly effective in synthesising the desired product and the reaction conditions for the preparation of the diethyl esters are given in Chapter 4.6, while the properties of the resulting products are shown in Tables 2 and 3. The hydrosilylations of these two disilyl protected mesogens however, proved unsuccessful.

Hydrosilylations may be possible by further increasing the alkyl chain of the mesogen, however, the longer chain bromoalkenes are expensive and the aim of the project was to keep the length of the alkyl portion of the backbone to a minimum. Therefore, an alternative protecting group had to be considered.

Fig.9 Preparation of Longer Chain Mesogens.

eg. $CH_2\ (CO_2Et)_2 + Na\ H$

$$\Big\downarrow \ \mathrm{DMF/0^{\circ}C}$$

$$^{-}CH\ (CO_2Et)_2$$

$$\Big\downarrow \ CH_2 = CHCH_2CH_2Br$$

$$CH_2 = CH(CH_2)_2\ CH(CO_2Et)_2$$

$$\Big\downarrow \ \mathrm{KOH/Ethanol}$$

$$CH_2 = CH(CH_2)_2\ CH(CO_2K)_2$$

$$\Big\downarrow \ H^{+}$$

$$CH_2 = CH(CH_2)_2\ CH(CO_2H)_2$$

$$\Big\downarrow \ (CH_3)_3SiCl/\mathrm{Pyridine}$$

$$CH_2 = CH(CH_2)_2\ CH(CO_2Si(CH_3)_3)_2$$

TABLE 2 Preparation of $CH_2 = CH(CH_2)_2\ CH(CO_2Si(CH_3)_3)_2$

Product	Boiling Point	Appearance	% Yield
(4-bromo-1-butene)	1) 99°C/760mm Hg	Colourless Liquid	-
Diethyl Ester	1) 70°C/0.5mm Hg 2) 250°C/760mm Hg	Colourless Liquid	83
Dicarboxylic Acid	-	White Solid	75
Disilyl Ester	1) 98°C/0.9mm Hg 2) 280°C/760mm Hg	Colourless Liquid	69

TABLE 3 Preparation of $CH_2 = CH(CH_2)_3CH(CO_2Si(CH_3)_3)_2$

Product	Boiling Point	Appearance	% Yield
(5-bromo-1-pentene)	1) 126°C/760mmHg	Colourless Liquid	-
Diethyl Ester	1) 93°C/1mm Hg 2) 270°C/760mmHg	Colourless Liquid	82
Dicarboxylic Acid	-	White Solid	79
Disilyl Ester	1) 130°C/0.8mm Hg 2) 330°C/760mm Hg	Colourless Liquid	67

3.3.3 The Hydrosilylation of Benzyl Esters

The benzyl group ($CH_2C_6H_5$) and a variety of substituted benzyl groups attached to an oxygen atom as in alcohols, ethers or esters, may be removed as toluene, or the correspondingly substituted toluene, by hydrogenolysis.

eg. $RCOOCH_2C_6H_5 + H_2 \rightarrow RCOOH + CH_3C_6H_5$

The hydrogenolysis may be accomplished by either chemical or catalytic means. Palladium is the favoured catalyst, but platinum (217-219), nickel (220,221) and copper chromium oxide (222-224) have also been used successfully. Chemical debenzylations have been affected by Raney nickel alloy (225), sodium amalgam, sodium in liquid ammonia (226-228) and lithium aluminium hydride (229).

The debenzylation of particular interest is the hydrogenolysis using palladium on charcoal (230-232), as deprotection is accomplished at ambient temperature and without the use of harsh acids or bases.

The mesogen chosen for preliminary studies was dibenzyl allylmalonate ($CH_2 = CHCH_2CH(CO_2CH_2C_6H_5)_2$), which was synthesised from dibenzyl malonate (see Chapter 4.6 for experimental details and Fig. 10).

Fig. 10 The Synthesis of Dibenzyl Allylmalonate.

(1) $H_2C\ (CO_2CH_2C_6H_5)_2 + NaH \rightarrow {}^-CH(CO_2CH_2C_6H_5)_2$

(2) ${}^-CH(CO_2CH_2C_6H_5)_2 + CH_2 = CHCH_2Br \rightarrow CH_2 = CHCH_2CH(CO_2CH_2C_6H_5)_2$

The dibenzyl allylmalonate (81% yield) was a colourless liquid having a boiling point of 168-172°C/0.2mm Hg. Dibenzyl allylmalonate was successfully hydrosilylated, under the conditions outlined in Chapter 4.2, resulting in the following product:

$Bu - (Si(CH_3)_2\ O)_n\ Si(CH_3)_2\ CH_2CH_2CH_2CH\ (CO_2CH_2C_6H_5)_2$

Deprotection of this hydrosilylated product, by catalytic hydrogenolysis (see Chapter 4.7 for experimental details), and the resulting sodium salt formation (see Chapter 4.10.3 for experimental details) produced a white crystalline solid. However, high resolution ^1H nmr indicated that the product was in fact the mono-salt and not the di-salt ie. there was no triplet observed at 3.45ppm relating to $-C\underline{H}\ (CO_2Na)_2$. It was therefore concluded that although the deprotection of the diacid was successful, decarboxylation also took place:

ie. $-CH\ (CO_2CH_2C_6H_5)_2 + H_2 \rightarrow - CH_2CO_2H$.

To verify these findings a hydrogenolysis was attempted on dibenzyl allylmalonate under the exact conditions employed on the hydrosilylated product. After hydrogen uptake had ceased and the work up was completed, ^1H nmr indicated that the product was the mono-acid ($CH_3CH_2CH_2CH_2CO_2H$). This was further verified by a titration with aqueous sodium hydroxide (see Chapter 4.8 for experimental details). Although the di-salts cannot be synthesised by this method, the synthesis of the mono-salts is possible and therefore the rest of the work concentrated on the synthesis of the afore mentioned di-salts but avoiding malonates.

From this work, it is obvious that, for the desired di-carboxyl functionalised siloxane to be synthesised, the two carboxylic acid groups of the mesogen had to be on separate carbon atoms. Therefore, benzyl protected itaconic acid, fumaric acid and maleic acid could prove to be ideal mesogens.

The esterification of acids can be achieved in many ways; most, however, use the appropriate alcohol. The esterification of acids with alcohols (233-238) can be accomplished only if means are available to drive the equilibrium in the desired direction. This can be achieved in a number of ways:

(1) addition of an excess of one of the reactants, usually the alcohol;
(2) removal of the ester or the water by distillation;

(3) removal of the water by azeotropic distillation;
(4) removal of water by use of a dehydrating agent or molecular sieve (239).

As previously stated, the use of an acid catalyst may lead to attack at the vinyl functionality. However, several methods utilising acid catalysts were used to convert itaconic acid to dibenzyl itaconate and it was noted that no such attack occurred.

Benzylation of itaconic acid was first attempted using a Dean-Stark apparatus, which allows azeotropic removal of the water by-product (see Fig.11). The reaction involves refluxing itaconic acid and benzyl alcohol in toluene with a catalytic amount of concentrated sulphuric acid. After water production had ceased the product was worked up, as described in Chapter 4.9.1.

Fig.11 Dean-Stark Benzylation Reaction.

$$CH_2 = C(CO_2H)(CH_2CO_2H) + 2\ C_6H_5CH_2OH \rightarrow CH_2 = C(CO_2CH_2C_6H_5)\ (CH_2CO_2CH_2C_6H_5) + 2H_2O$$

Although the desired dibenzyl itaconate was successfully isolated, an unknown contaminant was also present. Several methods were used to try and remove this contaminant but all proved unsuccessful. For a successful hydrosilylation the mesogen has to be free from all contaminants and therefore this method was inappropriate.

Another method using benzyl alcohol again utilised an acid catalyst (240). This method is similar to the Dean-Stark reaction detailed above, however, the water by-product is not removed. An excess of benzyl alcohol was refluxed with itaconic acid and a small amount of concentrated sulphuric acid for 12 hours. On work up (as described in Chapter 4.9.2) the desired dibenzyl itaconate was isolated.

A method that did not utilise an acid catalyst was desirable. An appropriate method proved to be the reaction of the di-salt of the acid with benzyl bromide in a dipolar aprotic solvent (see Fig.12). This type of reaction is well documented (241-244) and many reaction conditions can be employed (for a general method see Chapter 4.9.3).

Fig.12 Benzylation Using Benzyl Bromide.

eg.

$$CH_2 = C(CO_2Na)\ (CH_2CO_2Na) + 2C_6H_5CH_2Br \rightarrow CH_2 = C(CO_2CH_2C_6H_5)\ (CH_2CO_2CH_2C_6H_5) + 2Na\ Br$$

Many different salts can be used as starting material, including cesium (see Chapter 4.10.1), potassium (Chapter 4.10.2), sodium (Chapter 4.10.3), lithium and silver salts. Of the three itaconate salts synthesised here, the rate of reaction was found to be $Cs^+>K^+>Na^+$.

Alkylation of carboxylate salts with reactive organic halides has been demonstrated in non-polar (245,246) and polar solvents (247). With less reactive alkyl halides, the use of dipolar aprotic solvents is effective (248,249). It is noted that the reaction of the dicesium salt of itaconate acid with benzyl bromide in pure ethanol was unsuccessful, although other workers (249,250) have reported forcing the reaction between unactivated alkyl chlorides and carboxylate anions at elevated temperatures up to 165°C. The use of a dipolar aprotic solvent, however, proved highly effective. Pfeffer (241) found HMPA to be the most effective solvent for halogen displacement and the order of rates of reaction in various solvents is as follows: HMPA>NMP>Me_2SO>DMF. For the study carried out on itaconic acid salts, DMF proved effective and was used for all the reactions.

The final consideration was the nature of the benzyl halide. The order of reactivity of halogens in organic halides in S_N2 reactions is I>Br>Cl. The benzyl bromide was used and proved effective.

The method of reacting the di-salt of the acid with benzyl bromide was also used to synthesise dibenzyl fumarate (m.pt.55-57°C) and dibenzyl maleate (208-210°C/2.00mm Hg), as well as dibenzyl itaconate (b.pt. 180°C/0.5mm Hg).

A hydrosilylation reaction was attempted using the synthesised dibenzyl itaconate; this was unsuccessful. Three explanations, for this failure, were considered:

(1) The dibenzyl itaconate was impure;
(2) Steric hindrance resulted in the failure of the hydrosilylation (NB. dimethyl itaconate does hydrosilylate);
(3) The electron rich benzene ring affects the hydrosilylation process.

Impurities were considered the most likely reason for the failure. Therefore, a purification process was developed (see Chapter 4.11 for experimental details) and the resulting dibenzyl itaconate proved spectroscopically pure. However, an attempted hydrosilylation on the purified dibenzyl itaconate was still unsuccessful. Therefore, dibenzyl allylmalonate (which is known to hydrosilylate) was synthesised using the disodium salt of allylmalonic acid and benzyl bromide in DMF. The resulting crude dibenzyl allylmalonate was then purified (as in the method detailed in Chapter 4.11). A hydrosilylation of this dibenzyl allylmalonate proved successful thus proving that the purity of the dibenzyl itaconate was not a limiting factor. As a further check diethyl itaconate and dimethyl itaconate were both synthesised by the above method and hydrosilylations using these mesogens proved successful.

The next factor investigated was the steric effect. Although the benzyl group is bulkier than the methyl and ethyl groups, since it is "flat" it was thought that steric hindrance would not play a significant role. This observation was confirmed by synthesising diisopropyl itaconate and attempting a hydrosilylation reaction on it. The diisopropyl itaconate was synthesised by reacting itaconic acid with isopropyl alcohol in benzene with a small amount of concentrated sulphuric acid catalyst (see Chapter 4.9.2 for experimental details). The isopropyl protecting group is fairly bulky but the diisopropyl ester synthesised (b.pt.92°C/1.5mm Hg) was successfully hydrosilylated. Although not conclusive, this would indicate that the failure of the hydrosilylation of dibenzyl itaconate is not due to steric hindrance.

It was therefore concluded that the failure of the hydrosilylation of dibenzyl itaconate was due to the nature of the benzyl group; possibly due to its electron rich nature, combined with its position in the molecule with respect to the hydrosilylateable alkene group. As previously discussed, diethyl fumarate and diethyl maleate have been hydrosilylated. Dibenzyl fumarate and dibenzyl maleate were synthesised but, as expected, did not hydrosilylate.

The close proximity of the benzyl group, in benzyl protected itaconic, fumaric and maleic acids, to the reactive alkene site, resulted in the unsuccessful hydrosilylations. Therefore, for the hydrosilylation reaction to be successful the following criteria had to be met:

(1) the diacid had to be benzyl protected;

(2) the carboxyl functionalities should be bonded to separate carbons;

(3) neither carboxyl functionality should be attached to the carbon of the vinyl functionality.

The dibenzyl ester of 3-methylenepentanedioic acid ($CH_2 = C(CH_2CO_2CH_2C_6H_5)_2$) was considered to be a possible mesogen as it met all these criteria. The acid has been isolated from the reaction product of isobutylene, pentylsodium and carbon dioxide (251) but is usually prepared from the corresponding dicyano compound (252). However, the acid is thermally unstable and thus difficult to isolate in a pure form. Therefore, a reaction scheme (Fig.13) involving a Wittig reaction was attempted. The Wittig reaction involves the addition of a phosphonium ylide (eg. $RR^1C^- - P^+Ph_3$), also known as a phosphorane, to the carbonyl group of an aldehyde or ketone. Such species are generated by the reaction of an alkyl halide (RR^1CHX) on a trialkyl - or triaryl - phosphine (very often Ph_3P) to yield a phosphonium salt, followed by abstraction of a proton from it by a very strong base (eg. PhLi):

$$Ph_3P + RR^1CHX \rightarrow Ph_3P^+ - CHRR^1 \rightarrow Ph_3P^+ - {}^-CRR^1 \longleftrightarrow Ph_3P = CRR^1$$

Addition of this Wittig reagent to C = O results in the synthesis of the desired alkene after (usually spontaneous) elimination of a phosphine oxide from the intermediate.

Fig. 13 Proposed Reaction Scheme for the Preparation of the Dibenzyl Ester of 3-methylenepentanedioic Acid.

$$O = C\ (CH_2CO_2CH_2CH_3)_2 + Ph_3\ P^{+-}CH_2$$

$$\downarrow$$

$$CH_2 = C\ (CH_2CO_2CH_2CH_3)_2$$

$$\downarrow \ \text{KOH, EtOH, heat.}$$

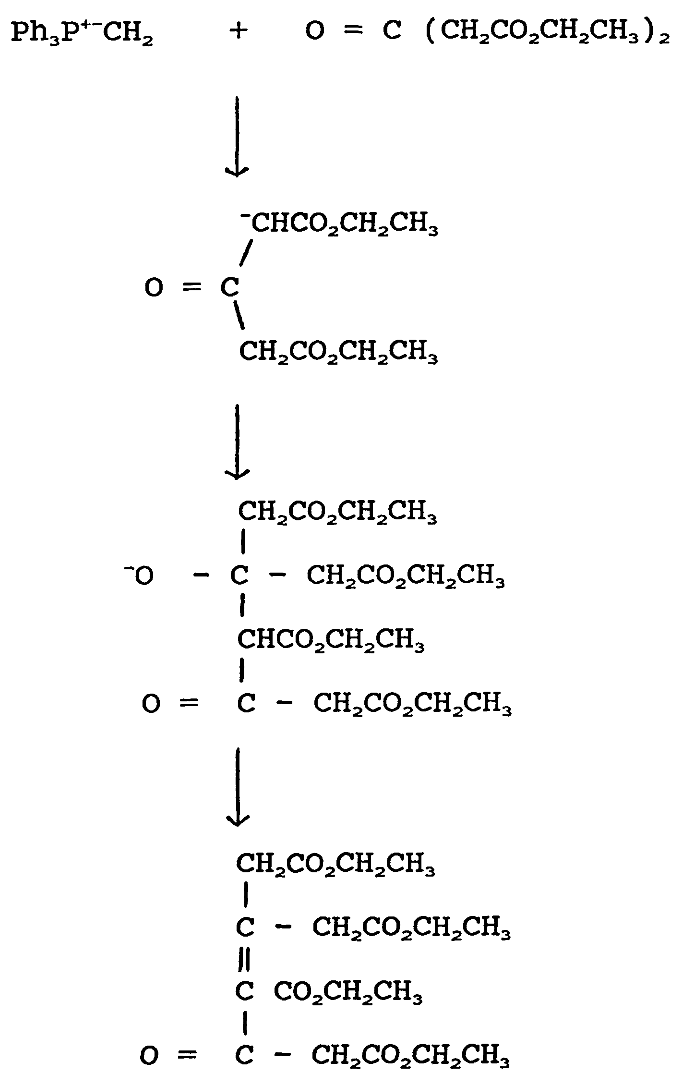
$$CH_2 = C\ (CH_2CO_2K)_2$$

$$\downarrow \ \text{Benzyl Bromide,DMF}$$

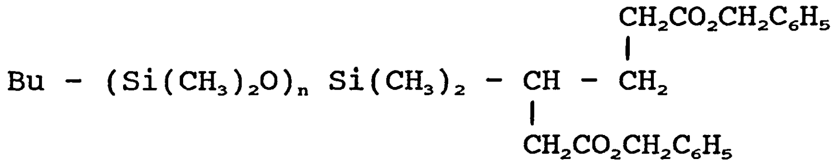
$$CH_2 = C\ (CH_2CO_2CH_2C_6H_5)_2$$

Therefore, a solution of phenyllithium in ether was reacted with triphenylmethylphosphonium bromide to form a phosphorus ylide. Diethyl - 1, 3-acetonedicarboxylate was then added (see Chapter 4.12 for experimental details). However, the product isolated was not the desired alkene. The reason for this failure was thought to be due to the highly acidic hydrogens of the two - CH_2 - groups adjacent to the carbonyl of the ketone. Since these hydrogens are adjacent to both a carbonyl of a ketone and of an ester their acidity is greatly increased and therefore, they are very susceptible to attack by a base. The 1:1 reaction carried out thus resulted in the removal of one of these acidic hydrogens followed by a Knoevenagel Condensation, which resulted in the product given in Fig.14. ^1H nmr and I.R. spectra, and mass spec. were used to characterise the product. To overcome this acidity problem a longer chain ketone, namely diethyl 4-oxopimelate ($O = C(CH_2CH_2CO_2CH_2CH_3)_2$), could be used.

Fig.14 Probable Reaction Path Taken



However, a commercially available mono-olefinic dicarboxylic acid, namely trans-3-hexenedioic acid ($HO_2CH_2CCH = CHCH_2CO_2H$), was considered a possible mesogen. The dibenzyl ester of trans-3-hexenedioic acid (m.pt. 34-36°C) was successfully synthesised using the conditions outlined in Chapter 4.9.2 and a hydrosilylation proved successful, resulting in the following product:



$$Bu - (Si(CH_3)_2O)_n\ Si(CH_3)_2 - \underset{\displaystyle CH_2CO_2CH_2C_6H_5}{\underset{|}{CH}} - \overset{\displaystyle CH_2CO_2CH_2C_6H_5}{\overset{|}{CH_2}}$$

Hydrogenation of this dibenzyl protected acid using hydrogen and a palladium catalyst proved highly efficient (see Chapter 4.7 for experimental details). The formation of the sodium salt was accomplished using an alcoholic solution of sodium ethoxide (see Chapter 4.10.3 for experimental details), which was added dropwise at a low temperature to eliminate the possibility of hydrolysis of the siloxane polymer. After filtration, the salt was purified and isolated using the method detailed in Chapter 4.15. IR and ^1H nmr spectra and micro-chemical analysis were used to characterise the product.

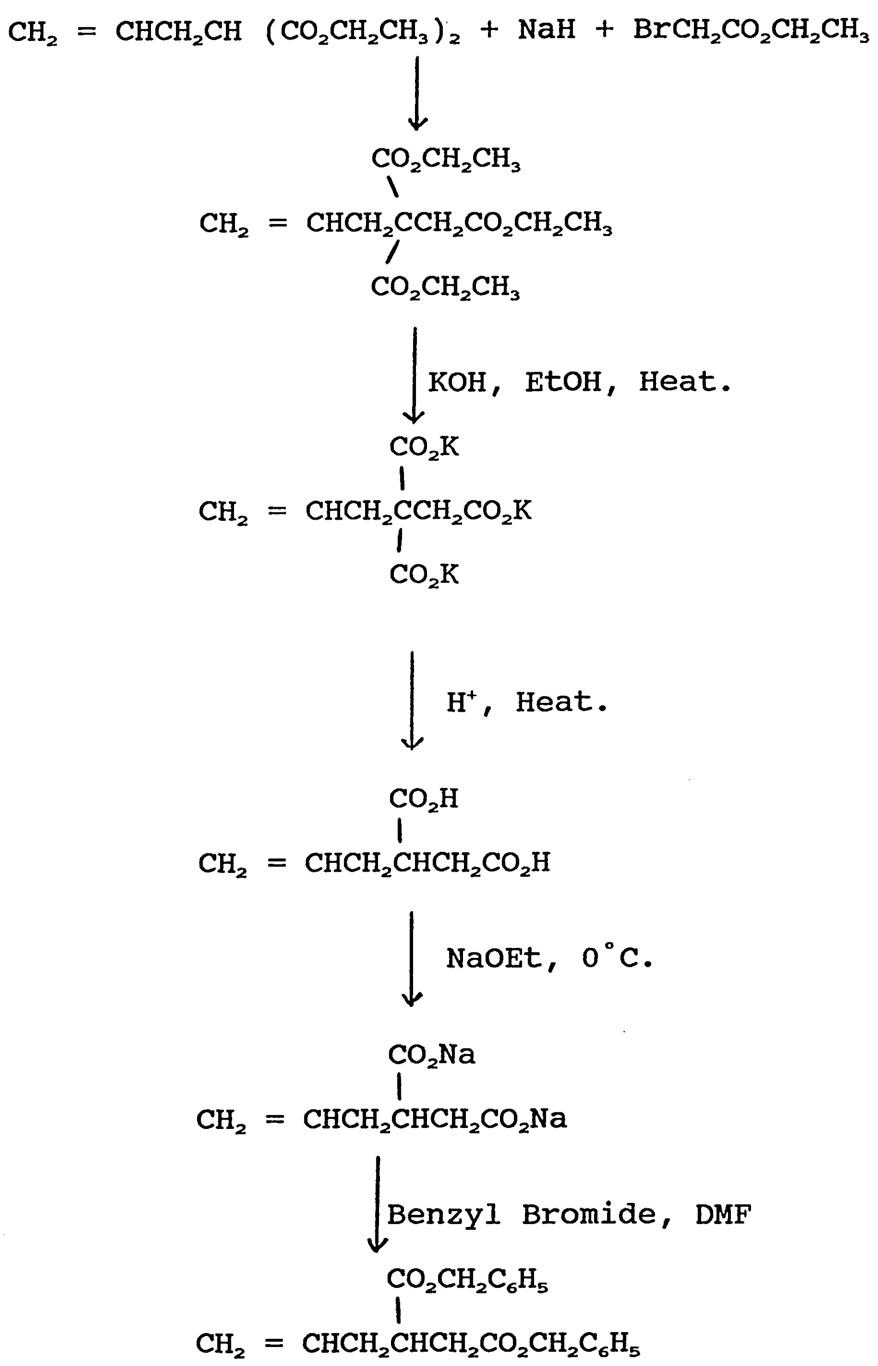
Dibenzyl allylsuccinate ($CH_2 = CHCH_2CH(CO_2CH_2C_6H_5)CH_2CO_2CH_2C_6H_5$) was also successfully hydrosilylated. Its synthesis was a five step process and the reaction scheme chosen is shown in Fig.15. Diethyl allylmalonate was converted to the triethyl ester, shown in Fig.15, using sodium hydride and ethyl bromoacetate (see Chapter 4.6 for experimental details). This was subsequently converted to the tripotassium salt (see Chapter 4.10.2 for experimental details) and then to allylsuccinic acid by acidification and heating. The dibenzyl protected acid was then prepared from the disodium salt of allylsuccinic acid (see Chapter 4.9.3 for experimental details), (b.pt.190°C/0.45mm Hg).

Finally, benzyl vinylacetate ($CH_2 = CHCH_2CO_2CH_2C_6H_5$) was synthesised and successfully hydrosilylated. After hydrogenolysis and salt formation the following compound was isolated in pure form (as well as the calcium salt equivalent):

$Bu - (Si(CH_3)_2O)_n\ Si(CH_3)_2\ CH_2CH_2CH_2CO_2Na$ where $n = 3\text{-}21$.

Therefore, the syntheses of the novel mono- and di- salt siloxane surfactants were successful. The physical characterisation of these products is outlined in Chapter 6. It is noted that all the products synthesised were verified by at least ^1H nmr and I.R. spectra and these details are given in Chapter 4.

Fig.15 Preparation of Dibenzyl Allylsuccinate.



$CH_2 = CHCH_2CH(CO_2CH_2CH_3)_2 + NaH + BrCH_2CO_2CH_2CH_3$

$$\downarrow$$

$CH_2 = CHCH_2C(CO_2CH_2CH_3)_2CH_2CO_2CH_2CH_3$

$$\downarrow \text{KOH, EtOH, Heat.}$$

$CH_2 = CHCH_2C(CO_2K)_2CH_2CO_2K$

$$\downarrow \text{H}^+\text{, Heat.}$$

$CH_2 = CHCH_2CH(CO_2H)CH_2CO_2H$

$$\downarrow \text{NaOEt, 0°C.}$$

$CH_2 = CHCH_2CH(CO_2Na)CH_2CO_2Na$

$$\downarrow \text{Benzyl Bromide, DMF}$$

$CH_2 = CHCH_2CH(CO_2CH_2C_6H_5)CH_2CO_2CH_2C_6H_5$

3.4 Alternative Synthetic Routes

3.4.1 Introduction

A vast amount of work was done on finding a suitable protecting group for the carboxylic acid functionality. Although a suitable protecting group was established, other synthetic methods were investigated with a view to synthesising the novel siloxane surfactants previously discussed. Three such alternatives were studied and although none of them were successful they are outlined briefly here.

3.4.2 The Hydrosilylation of Cyano Mesogens.

Many mesogens containing a cyano functionality have been successfully hydrosilylated (186). It was thought that if a suitable cyano mesogen could be found, then the conversion of the cyano group to the carboxylic acid group may be possible without damaging the siloxane backbone. The conversion of a cyano to a carboxylic acid functionality can be achieved in a number of ways, for example:

(1) Using H_2O and H_2SO_4 (253,254).

(2) Using H_2SO_4, $NaNO_2$ and H_2O (255).

(3) Using NaOH, EtOH and H_2O (256).

Before considering a dicyano mesogen, preliminary studies were carried out on an appropriate mono-cyano compound ie. allyl cyanide ($CH_2 = CHCH_2CN$). The proposed reaction scheme is outlined in Fig.16. Although allyl cyanide is available commercially, the conversion of vinylacetic

Fig.16 The Attempted Preparation of Target Molecules via Cyano Mesogens.

$$CH_2 = CHCH_2\ COOH$$

$$\Big\downarrow\ ClSO_2NCO/HCON(CH_3)_2$$

$$CH_2 = CHCH_2CN$$

$$\Big\downarrow\ \text{Hydrosilylation}$$

$$Bu - (Si(CH_3)_2O)_n\ Si(CH_3)_2\ (CH_2)_3\ CN$$

$$\Big\downarrow$$

$$Bu(Si(CH_3)_2O)_n\ Si(CH_3)_2\ (CH_2)_3\ COOH$$

$$\Big\downarrow\ NaOEt, 0^\circ C$$

$$Bu(Si(CH_3)_2O)_nSi(CH_3)_2(CH_2)_3COONa$$

acid to allyl cyanide was attempted to verify the reaction of Lohaus (257), with a view to the conversion of diacids into the analogous dicyano mesogen (see Chapter 4.13 for experimental details).

The hydrosilylations of allyl cyanide, using the method outlined in Chapter 4.2, were successful. The standard methods for the hydrolysis of -CN to -COOH utilise either acids or bases. As previously discussed, the use of a strong base breaks up the siloxane backbone, therefore the method of Adams (254), using water and sulphuric acid, was attempted (see Chapter 4.14 for experimental details). However, the acidic conditions resulted in the breaking of the Si-O bonds and therefore this method of synthesising the desired products could not be used.

3.4.3 The Hydrosilylation of Anhydrides

The hydrolysis of an anhydride can be accomplished under very mild conditions resulting in the formation of a dicarboxylic acid eg. itaconic anhydride on hydrolysis gives itaconic acid (258,259). Therefore, it was considered that this mild hydrolysis could be utilised, after hydrosilylation, to produce the required dicarboxylic acid siloxane.

Since diethyl maleate and dimethyl itaconate have both been hydrosilylated, maleic anhydride and itaconic anhydride were considered potential mesogens (See

Fig.17). Both anhydrides are insoluble in toluene and may be hydrolised by propan-2-ol, therefore, the hydrosilylation method employed was that detailed in Chapter 4.5. Unfortunately, the hydrosilylations of these anhydrides did not proceed.

The hydrosilylation of internal alkene bonds is notoriously difficult (216) and therefore the failure of the maleic anhydride hydrosilylation was expected.

The failure of the hydrosilylation of itaconic anhydride was presumably due to steric hindrance. The terminal vinyl group is directly bonded to the fairly rigid cyclic anhydride structure. During hydrosilylation a complex is formed about this double bond and the rigidity of the structure probably would not allow for the formation of this square planar complex (see Chapter 3.3 for the mechanism of the hydrosilylation reaction), resulting in the failure of the hydrosilylation.

It is noted that a potentially more suitable anhydride, which may be a feasible mesogen, is allylsuccinic anhydride. This can be synthesised from maleic anhydride (260).

Fig.17 Maleic Anhydride Itaconic Anhydride

3.4.4 Alternative to the Hydrosilylation Reaction.

Although it is widely accepted that hydrosilylation is the most effective route to the formation of a Si-C bond, an alternative synthesis was considered. It was reported by Sommer (261) that if sodiomalonic ester is heated with iodomethylpentamethyldisiloxane, the product is the disiloxanediester:

$$\mathrm{ICH_2(CH_3)_2\,SiOSi(CH_3)_3 + {}^{-}CH(CO_2C_2H_5)_2 \rightarrow (CH_3)_3\,SiOSi(CH_3)_2\,CH_2CH(CO_2C_2H_5)_2}$$

Therefore, the following reaction scheme was proposed:

$$\mathrm{Bu\text{-}(Si(CH_3)_2O)_{n-1}\,\text{-}Si(CH_3)_2\,OH + ClSi(CH_3)_2CH_2Cl \rightarrow Bu\text{-}(Si(CH_3)_2O)_nSi(CH_3)_2CH_2Cl}$$

then

$$\mathrm{Si(CH_3)_2\,CH_2Cl + NaCH(CO_2CH_2CH_3)_2 \rightarrow Si(CH_3)_2CH_2CH(CO_2CH_2CH_3)_2}$$

The reaction of the silanol with chloro(chloromethyl) dimethylsilane (see Chapter 4.1 for experimental details) proved successful. However, the subsequent reaction proved unsuccessful. By using the more reactive bromo- or iodo- dimethylsilane the reaction may proceed. However, these reactions were not attempted as the problems of deprotection would still have to be addressed (see Chapter 3.3 for details).

4. Experimental

Analytical Instruments

Infra-red spectra were run on a Pye-Unicam SP3-100 spectrophotometer. Samples were prepared as liquid films or potassium bromide (KBr) discs. ^{1}H nmr spectra were recorded on a Joel PMX 60 SJ spectrometer. Samples were prepared in the solvent stated in each method. Microanalyses were determined at Brunel University, London. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. Low resolution mass spectra were recorded on a VG Micromass 30F spectrometer. I.R. data is given in cm^{-1}. NMR data is given on the δ scale using tetramethylsilane as the internal reference. Abbreviations used for the form of the signal are as follows: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet and br=broad peak.

Thin-layer chromatography was performed on Merck 5554 Alufolien Kieselgel 60F$_{254}$ plates.

Solvents

Dry DMF was obtained by heating over calcium hydride followed by distillation under reduced pressure onto 4A molecular sieves. Dry THF was obtained by distillation from potassium metal. Dry diethyl ether was obtained by distillation from LiAlH$_4$ and storage over sodium metal. Dry pyridine was obtained by storage over potassium hydroxide. Dry toluene was obtained by storage over sodium metal. Dry benzene was obtained by storage over sodium metal. Dry dichloromethane was distilled from calcium hydride and stored over 4A molecular sieves. Dry methanol was distilled from sodium (after methoxide formation). Dry propan-2-ol was obtained by refluxing over calcium oxide followed by distillation onto 5A molecular sieves. Dry ethanol was obtained by refluxing over calcium hydride followed by distillation onto 4A molecular sieves. Dry acetonitrile was obtained by shaking with 4A molecular sieves, stirring with calcium hydride and then fractionally distilling. Dry acetone was obtained by storage over calcium sulphate and then distillation onto 4A molecular sieves.

Materials

All chemicals were used as supplied, except where stated. Sodium hydride was obtained as a 60% dispersion in mineral oil. n-Butyl lithium in hexanes was standardised with 2,5-dimethoxybenzyl alcohol, before use. Hyflo supercel filter aid was obtained from BDH chemicals.

4.1 The Synthesis of α-Si-H Functionalised Siloxanes (eg. 12 unit Siloxane)

Hexamethylcyclotrisiloxane (50g,0.225 moles) in freshly distilled, dry THF (50g) was added to a stirred solution of butyllithium in hexanes (35.13cm^3, 1.6M,0.056 moles) under a nitrogen atmosphere, at 0°C. The reaction mixture was stirred, at 0°C, for 20 hours and the living polymer was then end-protonated by the addition of deionized water (50% molar excess). A white precipitate formed immediately. The reaction mixture was then allowed to reach room temperature and was stirred for a further two hours. The THF was removed under vacuum and 40/60 petroleum spirit added to form a 10% (v/v) solution. The solution was filtered to remove the white precipitate and any other insoluble matter. The filtrate was dried over magnesium sulphate, filtered and the solvent removed under reduced pressure. The resulting 12 unit silanol was a colourless liquid. IR (liquid film) 3400 br, 2980, 1270, 1100, 1040 and 800. ^{1}H nmr ($CDCl_3$) O (s,66H), 0.80 (s,6H), 1.17 (m,9H) and 2.60 (s,1H).

The silanol (48g, 0.05 moles) was placed in a dry flask and dimethylchlorosilane (10% molar excess) was added. The vessel was sealed and allowed to stand, at room temperature, for one hour. The contents of the flask were filtered and the filtrate reprecipitated from acetone/water (80/20) (3 times) and dried over magnesium sulphate. The desired α-Si-H functionalised siloxane proved to be a colourless liquid. IR (liquid film) 2980, 2140, 1270, 1100, 1040, 915 and 800. ^{1}H nmr ($CDCl_3$) O(s,72H), 0.80(s,6H), 1.17(m,9H), and 4.66(m,1H).

4.2 The Hydrosilylation of Methyl and Ethyl Esters

All apparatus was flame dried and wrapped in foil to exclude moisture and light from the reaction. The hexachloroplatinic acid catalyst solutions in dry propan-2-ol (2ml) were made up in a dry nitrogen box and used immediately.

The mesogen (10% excess with respect to Si-H) and the functionalised siloxane were dissolved in dry toluene, and then an appropriate amount of the platinum catalyst solution (such that the molar ratio of catalyst to alkene was $1:10^4$) was added. The mixture was stirred, under a nitrogen atmosphere, at 80°C. The progress of the reaction was followed by monitoring the decrease in intensity of the Si-H infra-red adsorption at $2140cm^{-1}$. A small sample of the reaction mixture was withdrawn at intervals and the solvent evaporated off. The residue was placed between sodium chloride plates for analysis. The reaction was considered finished after the complete disappearance of the SiH peak (at $2140cm^{-1}$) on the IR spectra.

It is noted that the reaction may also be monitored by ^1H NMR spectroscopy (189). However, the Si-H and $CH_2 = CH-$ groups have similar chemical shifts (in the range 4.5-5.5) and this precludes a quantitative interpretation.

After the reaction was complete the toluene was removed under pressure and the resulting product reprecipitated from acetone/water (80/20) five times. The colourless liquid product was dried in vacuum. IR and ^{1}H nmr were used to characterise the various products.

4.3 De-esterification Reactions.

4.3.1 Using Potassium Hydroxide.

Potassium hydroxide (10.5g, 0.187 moles) was dissolved in distilled water (11ml) and ethanol (35ml) was added. Diethyl allylmalonate (13.8g, 0.07 moles) was introduced dropwise with shaking and the reaction mixture was refluxed for 2.5 hours. After refluxing, the ethanol was removed under pressure and the resulting precipitate was dissolved in a minimal amount of distilled water. The solution was cooled in ice and dilute sulphuric acid was added until the solution was acid to congo red. The solution was extracted with ether (3 x 100ml) and the solution dried over sodium sulphate. The ether was removed using a high vacuum pump (ie. no heat was used) and the resulting white solid was dried in a vacuum desiccator over anhydrous calcium chloride and silica gel. Yield 70%. Melting Point 102-105°C.(lit. value 103 - 105°C (262)). IR (KBr) 2500-3200 br, 1700 br, 1420, 930 and 790. ^{1}H nmr (D_2O) 2.60(t,2H), 3.65(t,1H), 4.76(s,2H), 5.09(t,2H) and 5.76(m,1H).

4.3.2 Using Sodium Hydroxide

The hydrosilylated product (from the reaction of dimethyl itaconate with the α-Si-H functionalised siloxane) was dissolved in a solution of ethanol/water (50/50). Sodium hydroxide (2.2 moles equiv.), in a minimal amount of water, was added dropwise, with stirring, at no more than 40°C. Water was added, as required, to maintain a homogenous solution. After the complete addition of the sodium hydroxide solution, the reaction mixture was acidified rapidly. The product was extracted into ethyl acetate and dried. After filtration and solvent removal the product was found to be a complex mixture. I.R., ^{1}H nmr and T.L.C. studies indicated that the siloxane backbone had in fact been broken and therefore, this method of deprotection proved inappropriate.

4.3.3 Using Chlorotrimethylsilane and Sodium Iodide.

A mixture of diethyl allylmalonate (8.02g, 0.04 moles) and chlorotrimethylsilane (13.04g, 0.12 moles) was stirred in the presence of anhydrous sodium iodide (17.99g, 0.12 moles) in dry acetonitrile (30ml) at a temperature of 70°C, for 20 hours. After 20 hours, the contents of the flask were filtered and water was added to the filtrate and stirred for 4 hours. The reaction mixture was taken up in ether and washed with water and then sodium thiosulphate solution to remove inorganic salts and iodine respectively. The ether layer was washed with brine and dried over sodium sulphate. After filtration, the ether was removed using a vacuum pump (ie. no heat was used) to yield a brown oil. ^{1}H nmr and I.R. data proved that the desired product had not been prepared.

4.4 The Disilyl Protection of Mesogens.

eg. Fumaric Acid

To a stirred solution of fumaric acid (5.0g, 0.043 moles) in dry THF, was added, under a nitrogen atmosphere, chlorotrimethylsilane (10.3g, 0.095 moles, 10% excess with respect to acid groups). Dry pyridine (7.5g, 0.0955 moles) was added and stirring was continued for 60 minutes. The reaction mixture was cooled in ice then filtered three times in a dry nitrogen atmosphere. The solvent was removed under reduced pressure and the resulting crude product vacuum distilled to yield the desired pure disilyl protected product. Melting point 60-62°C (lit. value 63°C (263)). I.R. (KBr) 2980, 1700 br, 1175, 970, 860 br, and 740. ^{1}H nmr ($CDCl_3$) 0.33 (s,18H) and 6.57 (s,2H). MS m/z 295, 147, 143, 73 and 95.

4.5 The Hydrosilylation of Disilyl Protected Mesogens

All apparatus was flame dried and wrapped in foil to exclude moisture and light. The hexachloroplatinic acid catalyst solutions in freshly distilled, dry THF (2ml) were made up in a dry, nitrogen box and used immediately. The disilyl protected mesogens (10% excess with respect to Si-H) and the siloxane were dissolved in dry THF, and the appropriate amount of the Pt catalyst solution (such that the molar ratio of catalyst to alkene was $1:10^4$) was added. The mixture was stirred, under a dry nitrogen atmosphere, for 7 days at 40°C. The THF was removed under pressure and the resulting product reprecipitated from acetone/water (80/20) five times. The product was dried in vacuo. I.R. and ^1H nmr were used to characterise the various products.

4.6 The Synthesis of Long Chain Diester Mesogens.

eg. $CH_2 = CH(CH_2)_3\ CH(CO_2CH_2CH_3)_2$

Diethyl malonate (8.70g, 0.054 moles) in freshly distilled, dry DMF, was added dropwise to a stirred solution of sodium hydride (2.61g, 0.065 moles) in DMF, at 0°C. The mixture was stirred, at 0°C, for one hour and then 5-bromo-1-pentene (9.69g, 0.065 moles) in DMF was slowly added. Stirring was continued at room temperature overnight. Cold water (50cm^3) was added and the reaction mixture extracted with ether (2 x 100 ml). The combined ether layers were washed with water (6 x 50 ml) and dried over magnesium sulphate. After filtration the ether was taken off on a rotary evaporator. The crude product was vacuum distilled to yield a colourless liquid, which proved to be the desired diester. I.R. (liquid film) 3100, 2980, 1720, 1645, 870, 770 and 730. ^1H nmr ($CDCl_3$) 1.27 (t,6H), 1.66 (m,6H), 3.40 (t,1H), 4.10 (q,4H), 4.83 (t,2H) and 5.63 (m,1H).

4.7 General Method of Deprotection by Catalytic Hydrogenolysis.

The dibenzyl protected siloxane (eg. 7.00g, equivalent to 0.0106 moles of ester bonds) was dissolved in 120ml of a 50:50 mixture of dry dichloromethane and dry ethanol, in a 250ml round bottom flask. The contents of the flask were purged for 15 minutes with dry nitrogen gas. After addition of the catalyst (5% Pd on charcoal, eg. 0.3118g), the flask was screwed onto the hydrogenolysis rig. After uptake of hydrogen had ceased the reaction was considered complete and the contents of the flask were filtered through filter aid and the ethanol and dichloromethane removed. The resulting product was reprecipitated from acetone/water (80/20) and dried in a vacuum desiccator over silica gel for a week. I.R. and ^{1}H nmr were used to characterise the various products deprotected by this method.

4.8 Titration of the Product from the Debenzylation of Dibenzyl Allylmalonate

The product from the debenzylation of dibenzyl allylmalonate (0.2085g) was dissolved in 100ml of distilled water (+ small amount of ethanol to aid dissolution). The solution was titrated with a standardised sodium hydroxide solution (0.0978 M) using phenolphthalein as indicator.

Amount of NaOH added was 20.88cm^3.

$$\text{Equivalent weight} = \frac{\text{grams of acid}}{(\text{volume of base consumed in litres})\ (N)}$$

where N = normality of
the standardised base.

$$\text{Equivalent weight} = \frac{0.2085}{(0.02088 \times 0.0978)}$$

<u>Equivalent weight = 102.10</u>

The relative molecular weight of $CH_3CH_2CH_2CH_2CO_2H$ is 102.13 (264), therefore, verifying the decarboxylation of the diacid.

4.9 Benzylation Reactions of Itaconic Acid

4.9.1 Azeotropic Distillation (Dean-Stark Method)

A mixture of itaconic acid (25g, 0.1920 moles), benzyl alcohol (45.70g, 0.4227 moles; 10% excess), toluene (150ml) and concentrated sulphuric acid (10 drops) was placed in a 3-necked round bottomed flask which was attached to a Dean-Stark trap and reflux condenser. The flask and Dean-Stark trap were lagged with glass wool and aluminium foil. The contents of the flask were refluxed. After water collection had ceased the solvent was removed on a rotary evaporator to yield a dark brown viscous liquid that was dissolved in ether and refluxed with activated charcoal for 15 minutes. After filtration through filter aid, the solvent was removed and a pale yellow product remained. ^1H nmr and T.L.C. indicated that the desired product was present, although it was contaminated with benzyl alcohol, as well as an unknown material. The benzyl alcohol was removed by vacuum distillation (b.pt. 70°C/10mm Hg) and the dibenzyl itaconate (b.pt. 180°C/0.5mm Hg) was vacuum distilled to yield a pale yellow product. This product, however, still contained an unknown contaminant.

4.9.2 Using Benzyl Alcohol/Sulphuric Acid

A mixture of itaconic acid (16.25g, 0.125 moles), benzyl alcohol (43.26g, 0.4 moles), benzene (100ml) and concentrated sulphuric acid (1.1ml) was placed in a 250 ml round bottomed flask and refluxed for 12 hours. The mixture was poured into water (250ml) and the benzene layer was washed with water (twice), saturated sodium hydrogen carbonate solution (twice) and water again (twice), then dried over anhydrous sodium sulphate, filtered and the solvent removed under reduced pressure. The resulting pale yellow liquid was purified by vacuum distillation to yield the colourless dibenzyl itaconate. Boiling point 180°C/0.5mm Hg. Yield 82%. I.R. (liquid film) 3100, 3080, 3045, 2985, 2900, 1730 br, 1640, 1610, 1590, 750 and 705. ^1H nmr ($CDCl_3$) 3.57 (s,2H), 5.20 (s, 2H), 5.27 (s, 2H), 5.73 (s, 1H), 6.43 (s,1H). and 7.33 (s, 10H).

Dibenzyl fumarate: Melting point 55-57°C. Yield 87%. I.R. (liquid film) 3100, 3080, 2985, 2900, 1740, 1660, 750 and 710. ^1H nmr ($CDCl_3$) 5.12 (s, 4H), 6.80 (s, 2H) and 7.20 (s,10H). The structure of the dibenzyl fumarate was confirmed from the literature (265).

Dibenzyl maleate: Boiling Point 208-210°C (2.0mm Hg). Yield 74%. I.R. (liquid film) 3100, 3080, 2985, 2900, 1740, 1665, 745 and 705. ^1H nmr ($CDCl_3$) 4.93 (s, 4H), 5.97 (s, 2H) and 7.10 (s, 10H). The structure of the dibenzyl maleate was confirmed from the literature (266-269).

4.9.3 Using Benzyl Bromide

Disodium itaconate (17.0g, 0.0977 moles) was stirred with benzyl bromide (36.76g, 0.2149 moles) in dry DMF (150ml) overnight at room temperature. The contents of the flask were poured into water (250ml) and extracted with ether (2 x 250 ml). The combined ethereal solutions were washed with water (2 x 200ml), saturated sodium hydrogen carbonate solution (2 x 100ml), and water (2 x 250ml), then dried over sodium sulphate, filtered and the ether taken off under reduced pressure. Excess benzyl bromide was distilled off to yield the crude dibenzyl itaconate, which was washed with hexane to remove trace amounts of benzyl bromide. After vacuum distillation a colourless liquid was isolated. ^{1}H nmr and I.R. indicated that it was dibenzyl itaconate (see Chapter 4.9.2 for details). Yield 89%.

4.10 Salt Formation

4.10.1 The Preparation of Dicesium Itaconate

Itaconic acid (1.94g, 0.0149 moles) was dissolved in a mixture of methanol (100ml) and distilled water (10ml). The solution was titrated to pH 7 (pH paper) with a 20% aqueous solution of cesium carbonate. The mixture was evaporated to dryness and the residue re-evaporated twice from DMF (120ml). The white solid product was then dried in an oven to constant weight. An I.R. spectrum indicated that all the carboxylic acid functionality had been converted to the salt. Yield 71%. I.R. (KBr) 2980, 2935, 2900, 1635, and 1575.

4.10.2 The Preparation of Dipotassium Itaconate

Potassium hydroxide (10.5g, 0.19 moles) was dissolved in water (11ml), and ethanol (35ml) was added. Dimethyl itaconate (11.07g, 0.07 moles) was added dropwise with shaking and the contents of the flask were refluxed for 2 hours. After refluxing, the ethanol and water were removed on a rotary evaporator to yield a white solid which was stirred in dry ethanol overnight, filtered and dried in an oven to constant weight. An I.R. spectrum showed that the desired salt had been prepared. Yield 68%. I.R. (KBr) 2985, 2935, 2900, 1630 and 1575.

4.10.3 The Preparation of Disodium Itaconate

Itaconic acid (20g, 0.1537 moles) was dissolved in absolute ethanol (150ml) and cooled to 5°C. Thereafter, an ethanolic solution of sodium ethoxide, made by dissolving sodium (7.77g, 0.3381 moles) in ethanol (250ml), was added dropwise, under rapid stirring. A white precipitate was formed immediately. After total addition, the mixture was stirred for a further two hours at room temperature. The contents of the flask were filtered through a Buchner funnel at water-pump vacuum. The white salt was dried in an oven to constant weight. Yield 78%. I.R. (KBr) 2985, 2935, 2905, 1635 and 1570.

4.11 The Purification of Dibenzyl Itaconate

After removal of the unreacted benzyl bromide by vacuum distillation the residue was washed with dry hexane. The dibenzyl itaconate was then dissolved in dry ethanol and activated charcoal was added. After refluxing for one hour the hot solution was filtered through filter aid and the solvent removed on a rotary evaporator. The product was dissolved in dry ether and dried over anhydrous sodium sulphate. After filtration and removal of the ether, the resulting product was vacuum distilled to yield spectroscopically pure dibenzyl itaconate. I.R., ^{1}H nmr and T.L.C. were used to verify the identity and purity of the product.

4.12 The Attempted Preparation of the Diethyl Ester of 3-methylenepentanedioic Acid

An ethereal solution of phenyllithium was prepared from lithium wire (1.35g, 0.195 mol), dry redistilled bromobenzene (13g, 0.08 mol) and anhydrous ether (85ml). After the conversion to phenyllithium was complete the solution was diluted with a 15ml portion of anhydrous ether and decanted from any unreacted lithium into a clean 3-necked 250ml flask equipped with a nitrogen inlet, a solids addition funnel and a reflux condenser.

Triphenylmethylphosphonium bromide (26.80g, 0.075 moles) was added, at room temperature, in portions over 15 minutes. The suspension was stirred at room temperature for 4 hours. Diethyl-1,3-acetonedicarboxylate (15.17g, 0.075 moles) was added with vigorous stirring to effect solution. The reaction mixture was stirred overnight with heating, then water (25ml) was added. The precipitate was removed by filtration, washed with diethyl ether and the combined ether extracts dried over anhydrous sodium sulphate. The ether was removed on a rotary evaporator to yield a solid which was recrystallised from 40/60 petroleum spirit (melting point 79-82°C). ^{1}H nmr and I.R. indicated that the desired product had not been synthesised (see Chapter 3.3.3 for details). I.R. (KBr) 3000, 2940, 1730, 1660, 1530 and 1245. ^{1}H nmr ($CDCl_3$) 1.23 (t,12H), 3.07 (s,4H), 3.98 (m,8H) and 4.53 (s,2H).

4.13 The Synthesis of Allyl Cyanide

Vinylacetic acid (5.0g, 0.058 moles) in dry dichloromethane (25ml) was refluxed and chlorosulfonyl isocyanate (8.5g, 0.06 moles), in dry dichloromethane (20ml), was added slowly with stirring. After the addition was complete, the reaction mixture was refluxed for an hour. DMF (8.77g, 0.12 moles) was added over 15 minutes while cooling in ice and the reaction mixture was stirred for a further 15 minutes then poured onto crushed ice (50g); two layers formed. The layers were separated and the aqueous layer was extracted with dichloromethane (50ml). The dichloromethane layers were combined and washed with water (6 x 50ml) then dried over potassium carbonate overnight, decanted off and finally concentrated to the crude product at reduced pressure. The crude product was purified by distillation. Yield 72%. Boiling point 116-121°C. I.R. (liquid film) 3060, 2915, 2240, 1640, 1410, 900 and 870. ^1H nmr (CCl_4) 3.10 (d,2H), 5.10-5.65 (m,2H) and 5.77 (m,1H).

4.14 The Hydrolysis of the Cyano Group

A mixture of water (4ml), dilute sulphuric acid (3ml) and the hydrosilylation product (12 unit; 20g, 0.019 moles) was heated under gentle reflux, and stirred for 3 hours. The contents of the flask were poured into water (250ml) and extracted with ether (2 x 200ml). The combined ether layers were washed with water (2 x 200ml), saturated sodium hydrogen carbonate (150ml) and water (2 x 200ml) then dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure. The resulting product was reprecipitated from acetone/water (80/20). I.R. and ^1H nmr studies indicated that the desired acid had not formed (see Chapter 3.4.2 for details).

4.15 The Purification of the Linear Amphiphilic Siloxanes

The di-salt (0.5g) was placed in a 50ml round bottomed flask and dry acetone (10ml) was added. The flask was placed in a sonication bath for 10 minutes then the acetone was decanted off. This procedure was repeated a further four times. After the final sonication the acetone was taken off on a rotary evaporator to yield the purified product, which was dried in an oven to constant weight.

5. Experimental Techniques

5.1 Introduction

After synthesising the pure, target, ionic, polymeric surfactants, time allowed for only a brief overview of the phase behaviour of these materials. The majority of the work concentrated on the lyotropic behaviour of these amphiphilic materials.

The main techniques employed in the study of liquid crystals are:

(1) Optical polarising microscopy;
(2) Differential scanning calorimetry (DSC);
(3) Deuterium NMR spectroscopy and
(4) X-ray diffraction.

The information from one of these techniques is not sufficient alone to determine the nature of a given mesophase. Therefore, at least two techniques are usually required. As time was short, optical polarising microscopy and to a lesser extent differential scanning calorimetry were employed during this study. For a more thorough investigation all four techniques should be utilised.

The principles, experimental methods and apparatus used in optical polarising microscopy and differential scanning calorimetry will be discussed in detail in this chapter. Although deuterium NMR spectroscopy and X-ray diffraction studies were not utilised in this study a brief description of their uses will also be given.

5.2 Optical Polarising Microscopy

5.2.1 Introduction

A polarising microscope equipped with a heating stage permits visual observation of the phase transformations which occur when a compound passes through the liquid crystalline state as a result of changing either its temperature (thermotropic behaviour) or its concentration in an added solvent (lyotropic behaviour). Using such an instrument, simple observations of the morphology and orientation patterns displayed by a thin-film preparation of a liquid crystalline phase may be sufficient to establish its main structural type, but more detailed indications of structure will generally be gained by also determining its characteristic optical properties.

Hexagonal, lamellar and nematic lyotropic phases (described in Chapter 1) are anisotropic and when viewed under the crossed-polaroid of a polarising microscope show optical patterns characteristic of the particular mesophase present. The cubic phases are optically isotropic due to their three-dimensional order and therefore they do not show 'textures' under the polarising microscope. Rosevear (270) has described the textures of lamellar and hexagonal phases.

The technique of optical polarising microscopy provides the principal means of investigation of liquid crystal phases because of the simplicity of the experimental method and the amount of information thus obtained. It is therefore usually the first technique employed in investigations into both thermotropic and lyotropic liquid crystals.

The microscopes used in these studies were a Rekhart Neopan polarising microscope fitted with a Koffler hot stage and a Nikon Optiphot polarising microscope with a Linkam THS 600 hot stage and a Linkam THS 90 controller. The magnification of both microscopes was x100. See Fig.1 for a diagrammatic representation of a polarising microscope and Fig.2 for the principal components of the polarising microscope.

5.2.2 Polarised Light and Birefringence

Light can be considered as a series of waves perpendicular to the direction in which the beam is travelling. Although perpendicular, these waves can take any angle about the axis of propagation. Plane polarised light is produced when a beam is passed through a very narrow grating (polaroid). Only waves in the same plane as the gaps in the grating are allowed through, thus the resultant light vibrates in a single plane. If the beam is then passed through another polaroid filter placed in the same sense as the first, the light is again transmitted, but if the second filter is rotated through ninety degrees (crossed-polaroid) extinction occurs. Rotation between zero and ninety degrees results in partial extinction. Most transparent substances transmit light without changing the plane, and when they are placed between crossed polars the transmitted light is extinguished by the second polaroid. However, if a birefringent material is placed between crossed polars it is illuminated because the rotated light is allowed through the second polaroid, and distinctive 'textures' are observed.

As a result of their ordered molecular arrangement, most mesophases are said to be birefringent and this is the property used in microscope studies. The cause of birefringence can be explained, in simple terms, as follows: Fig.3a shows the simplest form of an elongated molecule, namely an atom pair, in different orientations with respect to the electric vector, ie. the vibration direction of the light. The action of the light waves is to displace the centres of gravity of the electron systems of the atoms in relation to their nuclei in the direction of the electric vector. The magnitude of this effect in a transparent medium increases with the vibrational frequency of the light and, therefore, decreases with the wavelength. Dipoles are thus produced as shown in the figure. In Fig.3a the light vibration is in the direction of the line joining the atoms and, as a result of induction, the strength of the dipoles will be greater than if the atoms were separated from one another. In Fig.3b the light is vibrating at right angles to the long axis of the molecule and the dipoles are side by side. Therefore, the effect of induction is to reduce the strength of the dipoles below the value they would have if the atoms were far apart. These conclusions can be broadly applied to complex elongated molecules such as those occurring in mesophases. Therefore, when the light is vibrating parallel to the long axis of such a molecule the average strength of the dipoles produced is in general greater than when it is vibrating across this axis. The optical properties of a mesophase in which such molecules are arranged parallel to one another (Fig.4a) will reflect closely those of the individual molecules, and so for a given wavelength the refractive index will be greater when the light is vibrating in the direction of the molecules than when it is vibrating in a transverse direction. Another feature of most mesophases of this kind is that both the lateral distribution of the molecules and their orientations about their long axes are random, so that the refractive index for light vibrating at right angles to the long axes is the same for all such directions. Fig.4b shows the case of a medium in which planar molecules are arranged parallel to one another.

5.2.3 Optical Textures of Liquid Crystals.

Liquid crystalline textures, viewed through cross polars, allow a rapid initial assessment of the mesophases present. Each mesophase has its own particular characteristics and properties, and these have been reported extensively (271-275). Therefore, only a brief description of these characteristics are given here.

The lamellar phase is birefringent and very mobile. When pressure is applied, the lamellar phase can be seen to flow easily and this pressure also destroys the order within the lamellar phase so causing it to go isotropic. Focal conical textures usually occur and the 'unit' textures often appear as spherulites (ie. small round patches of birefringence containing a dark maltese cross shape). The spherulites can be encountered individually or as part of a 'mosaic' texture. Other features that are indicative of lamellar phases are: myelins (birefringent "worm" like projections, from the edge of the lamellar phase), fans, batonnets and oily streaks. Any air bubbles trapped in the lamellar phase appear round.

The hexagonal phase is also birefringent but is more viscous and does not flow much under pressure. The most common texture observed is a 'fanlike texture'. Another type of structure observed is a non-geometric texture.

Because of its viscous nature any air bubbles trapped in the hexagonal phase are often distorted.

The cubic phase is recognisable because it is isotropic in appearance and very viscous. It does not flow at all when pressure is applied and air bubbles trapped in it are often extremely distorted in shape. The type of cubic phase formed is indicated by the concentration of surfactant at which it occurs, relative to other mesophases seen using the penetration scan technique (see Chapter 5.2.4).

The lyotropic nematic phase may be uniaxial or biaxial (276). The optical texture is analogous to the thermotropic nematic phase (ie. Schlieren texture) and its viscosity is the lowest of all the lyotropic mesophases.

5.2.4 Experimental Techniques

Samples can be studied both thermotropically and lyotropically. Thermotropic analysis involves looking at the sample through and without crossed polars, whilst heating. Observations of the texture and viscosity of bulk samples were achieved by constructing a thin sample film between a glass microscope slide and a cover-slip.

The majority of the work however, involved lyotropic studies. These studies involved a penetration technique

(277) which allows for an initial survey of the liquid crystals formed by a surfactant/solvent system. The penetration technique involves placing a small amount of the sample on a microscope slide and a cover-slip is then placed over the sample. An edge of the sample is then contacted with a small amount of an appropriate solvent so that a concentration gradient is established and the lyotropic mesophases may then develop as bands around the anhydrous sample. The system is then observed over an appropriate temperature range. The technique is useful as mesophases appear in order of surfactant concentration. However, penetration techniques only indicate which phases are formed; it is not specific with regard to the compositions at the mesophase boundaries. For these to be determined different samples of known composition would have to be made up and studied as a function of temperature.

Time only allowed for penetration studies to be carried out. However, as previously discussed, this technique is ideal in giving an overview of the liquid crystal mesophases formed in surfactant/solvent systems.

5.3 Differential Scanning Calorimetry.

5.3.1 Introduction

Differential scanning calorimetry (DSC) is used to detect and characterise thermally induced phase changes. The phase changes studied are first order, for example a solid melting to a liquid, or one liquid crystal mesophase melting to another. DSC complements the optical microscopy work and has found widespread use (278-284).

5.3.2 Principles and Experimental Techniques

DSC is carried out by heating the sample and a reference sample at the same rate and comparing the two. Modern types of DSC operate by the Null-Balance principle. Aluminium crucibles containing the sample and reference, are heated at the same rate by individual micro-furnaces. Platinum resistance thermometers are employed in measuring temperature and heating changes. When a thermal event (eg. a phase change) takes place, the temperature of the reference will be different to the study sample, this change is sensed and the power adjusted so that the equilibrium between the furnaces is regained.

The energy used in regaining the equilibrium, whether positive or negative, is directly proportional to the enthalpy change of the phase transition. Thus a trace is produced of change in temperature/energy (ie. heat flow) against time/temperature, which shows peaks corresponding to the enthalpy of the phase changes. The peaks can then be integrated and a simple calculation performed to give a value for the enthalpy of the phase change.

The range of temperatures used in DSC can vary between $^{-}170$-$^{+}900$°C, and can be of a heating or a cooling nature. The computerised control of the system provides a means of linking a series of heating and cooling runs, since the metastability of various phases gives rise to varying results on reheat/recool profiles. If metastable phases are not involved, the peaks seen on heating will be reversed on cooling (endothermic becomes exothermic and vice-versa). Most processes are endothermic (require energy input) on a heating profile.

The technique of DSC is useful as a preliminary form of analysis, as it gives a clear indication of the temperatures at which transitions occur and, since the enthalpies of these transitions are indicative of the type of process occurring, give an idea of the type of phase change.

5.4 Nuclear Magnetic Resonance Spectroscopy

5.4.1 General Theory

Many atomic nuclei behave as though they are spinning, and as a result of this spin they possess angular momentum and magnetic moments. Angular momentum is quantised in units of h, where h is Planck's constant divided by 2π. For the maximum observable component of angular momentum:

$$p = Ih \qquad (5\text{-}1)$$

The constant of proportionality, which is either an integer or half-integer, is given the symbol I and is referred to as the nuclear spin quantum number or the nuclear spin. Nuclei can therefore be classified according to their nuclear spins. There are a number of nuclei that have I = 0 and hence have no angular momentum. This class includes those with even atomic mass numbers eg. ^{12}C. These nuclei cannot experience magnetic resonance under any circumstances (285). Two nuclei relevant to this work are ^{2}H (where I = 1) and ^{23}Na (where I = 1.5).

Those nuclei with I>1 have non-spherical nuclear charge distribution and hence an electrical quadrupole moment, Q. All the nuclei with $I \neq 0$ possess a magnetic dipole moment, or a magnetic moment. When such a nucleus is placed in a static uniform magnetic field, H_o, it takes up one of (2I+1) orientations. If, for simplicity, the bare nucleus is a proton, which has a spin number I = 0.5, it can be likened to a very tiny bar magnet, the axis of which is coincident with the axis of spin of the spinning nucleus. Quantum mechanics tells us that the tiny proton magnet is restricted to just two possible orientations [(2I+1) = 2] in the applied field and these can be considered to be a low energy or parallel orientation in which the magnet is aligned with the field and a high energy or anti-parallel orientation in which it is aligned against the field. These two orientations correspond to two energy states and hence it should be possible to induce transitions between them. The frequency, ν , of the electromagnetic radiation which will effect such transitions is given by the equation:

$$h\nu = \frac{\mu \beta_N H_o}{I} \qquad (5-2)$$

Where β_N is a constant known as the nuclear magneton. The adsorption or the emission of the quantum energy, $h\nu$, causes the nuclear magnet to turn or flip from one orientation to another. For nuclei with spin numbers greater than 0.5 there will be more than two possible orientations (eg. 3 for I=1, 4 for I = 1.5 etc) and in each case a set of equally spaced energy levels result.

Returning to the nuclei with I=0.5; in the steady state the total energy of the nuclei in each level must be equal, or there would be an interchange to make it so. Hence, there must be a higher population of nuclei at the lower level. When radio frequency energy is applied the probability of a jump to the higher energy level is equalled by the probability of falling back, with consequent re-emission of radiant energy. But because there is a higher population at the lower level, there will be a greater adsorption of energy than emission, and the net adsorption can be measured (285,286).

A quadrupolar nucleus (I>0.5) interacts with the electric field gradients of its environment through the quadrupole moment. If such a nucleus 'tumbles' anisotropically, quadrupole splittings are observed in the NMR spectrum of that nucleus. For such a case, the first-order perturbation term corresponds to the splitting of the NMR signal into 2I symmetrical components. If, however, the quadrupole interaction is large enough, a second order perturbation and the corresponding spectral asymmetry are noticeable.

There is an orientation in liquid crystals, therefore, non-averaged electric field gradients are produced and nuclei which have electric quadrupole moments interact with the field gradient at the nucleus resulting in the splitting of the NMR resonance into the 2I peaks. For water deuterons (I=1) the electric field arises mainly from the O-D bond, and the magnitude of the splitting (Δ) is given by equation (5-3) for a powder sample (287-289):

$$\Delta = 1\Sigma_i P_i D_Q S_i 1 \qquad (5\text{-}3)$$

The values of Δ are a weighted average of the values at the different sites, i, due to rapid exchange, and S_i, the order parameter describing the orientation of the fraction of molecules at site i (P_i) is given by equation (5-4).

$$S_i = 0.5 \quad (3 \cos^2 \theta_{DM} -1) \qquad (5\text{-}4)$$

where θ_{DM} is the angle between the liquid axis (the director) and the electric field gradient.

Water molecules occupy different binding sites and these sites will have different binding energies. This leads to a relationship between Δ and concentration and also one site will have a larger splitting than another. For example water bound to head groups in an amphiphilic molecule is expected to have a larger quadrupole splitting than water bound to counter ions (287-289).

5.4.2 Application to Liquid Crystals

The more ordered the quadrupole nuclei are in their environment, the more the NMR signal is split. NMR is therefore used in phase determinations of liquid crystals, as they have different levels of order within them, and this gives a direct relationship between the Δ value and the phases.

The sizes of the splittings are measurable for different phases and NMR can also be used to examine how the D_2O is bonded within the phase, because the splitting produced will also be influenced by the angle of the D_2O molecule to the director.

For example, the order parameters of hexagonal and lamellar phases of the same system are directly related to each other, if the microscopic structure at the water-amphiphile interface can be assumed to be identical for the two phases. Thus if the molecular motion around the rods of the hexagonal structure proceeds in a short time compared to the inverse splitting, the splitting of the hexagonal phase should be half that of the lamellar phase (287-289).

5.5 X-ray Diffraction

5.5.1 General Theory

The fundamental basis for x-ray diffraction stems from the fact that electrons in a crystal will reflect x-ray photons. An x-ray beam passed through a crystalline sample produces a scattering pattern characteristic of the crystal's structure and symmetry, and directly related to the dimensions involved.

Common methods for the use of x-ray diffraction involve studies of a single perfect crystal to obtain molecular and crystal structure, and diffraction of powder (polycrystalline) samples to give structural information. X-ray diffraction of liquid crystal phases is equivalent to that of powder crystal samples since they contain discontinuities, due to the sample comprising of many small domains. X-ray patterns can be used to calculate the unit cell dimensions of a liquid crystal phase but not to distinguish between normal and reversed phases; this is carried out by other methods of analysis.

In a crystal lattice there are repeated units; in a normal crystal the structure can be considered as being built from these unit cells. A unit cell is defined as being the smallest unit from which the three dimensional lattice can be built. The unit cell can in turn be made up from a number of asymmetric units. There are therefore points in the lattice which can be considered as equivalent and these equivalent points act as a mirror plane.

Diffraction arises as a result of interference between waves. Where their amplitudes are in-phase the waves augment each other and the intensity is enhanced; where their amplitudes are out-of-phase they cancel, and the intensity is decreased (290).

The Bragg condition gives the relationship between the incident angle and the wavelength, which has to be satisfied for diffraction from a particular set of planes in order to give constructive interference (increased intensity):

$$n\lambda = 2d \sin \theta \qquad (5\text{-}5)$$

where n=integer; λ = wavelength of the incident beam; d= inter-planar spacing and θ = incident angle.

The Bragg condition can be achieved in a number of ways:

(1) by passing a beam covering a range of wavelengths through a single static crystal;

(2) by passing a monochromatic beam through a single crystal which can be rotated;

(3) by passing a monochromatic beam through a powder sample.

The diffraction pattern of a crystal is a three-dimensional array of points in space. This information is commonly collected using photographic paper sensitive to x-rays (electronic devices are also available for this purpose). A useful way of looking at diffracted rays is to modify the data by use of a mathematical transform, this can be performed by computer using a Fourier Transform process, or by an optical device. In practice, photographs of diffraction patterns from stationary crystals are not used, instead the crystal is rotated in a precise manner in order to generate a pattern.

Diffraction patterns have a reciprocal relationship with the object, in effect large features in the crystal structure give rise to small features in the diffraction pattern, and vice versa.

5.5.2 Application to Liquid Crystals

X-ray diffraction by a liquid crystal is equivalent to that of powder samples. Liquid crystals are studied using low angle, rather than high angle x-ray diffraction methods, simply because the data produced is related to the long range dimensions, and not small features such as bond lengths. Different phases can be identified by their diffraction lines:

(1) Lamellar: Produces lines in the ratio d:d/2 : d/3 : d/4 and have one dimensional periodicity. $d=d_o$, where d_o is the unit cell dimension (ie. the thickness of the water layer plus the surfactant bilayer thickness).

(2) Hexagonal: Produces lines in the ratio d:d/3 : d/4 : d/7, where d is the separation between adjacent rows of rod micelles. The hexagonal phase has two dimensional periodicity (other phases with two dimensional periodicity have been suggested (291)).

(3) Cubic: Produces a range of patterns, eg. d/4 : d/5 : d/6 : d/8 : d/10. However, normally only the first few lines are observed (292, 293).

An important aspect of low angle x-ray diffraction is its ability to assist calculation of the head group area. This is needed in packing constraint theory, and useful in understanding anomalies in phase behaviour in terms of modification of the expected head group area eg. salt impurity can effectively reduce the head group size.

In order to calculate the unit cell size or dimensions of the water region, consider a sample containing M moles of surfactant per gram of sample (see equation 5-6), where

Z is the percentage of surfactant by weight and S is the molar mass of the surfactant.

$$M = Z/100.\ S \qquad (5\text{-}6)$$

It is assumed that the head groups (molar mass = G) reside in the water (density = P_w), separated from the non-polar parts (molar mass = H, density = P_h). Such that H + G = S.

The weight fractions of the aqueous (Z_w) and the non-polar (Z_h) regions are :

$$Z_h = (H.Z)/S.100 \qquad (5\text{-}7)$$

$$Z_w = ((100-Z) + (G/S).Z)/100 \qquad (5\text{-}8)$$

$$= (1 - Z_h) \qquad (5\text{-}9)$$

The volume fraction of the non-polar region (ϕ_h) is:

$$\phi_h = (Z_h/P_h) / ((Z_h/P_h) + (1-Z_h)/P_w) \qquad (5\text{-}10)$$

The structure of the mesophase is then taken into account:

(1) The Lamellar Phase (284,285):

The thickness of the non-polar region (d_h) is:

$$d_h = \phi_h\ .\ d_o \qquad (5\text{-}11)$$

Similarly, for the aqueous thickness (d_w):

$$d_w = \phi_w\ .\ d_o \qquad (5\text{-}12)$$

$$= (1 - \phi_h)\ d_o$$

For the area per surfactant head group, a, a bilayer structure is assumed. The volume of a one gram sample is therefore:

$$Z_w/P_w = Z_h/P_h \qquad (5\text{-}13)$$

This has a total bilayer thickness:

$$(2/d_o) \,.\, (Z_w/P_w + Z_h/P_h) \qquad (5\text{-}14)$$

This is divided by the number of moles per surfactant (M) and Avogadro's number (N), to give the area per molecule $\underline{a}$ (in Å^2):

$$\underline{a} = ((2/d_o) \,.\, (Z_w/P_w + Z_h/P_h) \,.\, (10^{24}/(M.N)) \qquad (5\text{-}15)$$

(2) The Hexagonal Phase (296,297):

The centre-centre separation is calculated first:

$$d_o = 2d/\sqrt{3} \qquad (5\text{-}16)$$

The non-polar radius, r_h, is given by:

$$r_h^2 = (2d^2/\pi\sqrt{3}) \,.\, \phi_h \qquad (5\text{-}17)$$

The minimum water thickness is $d_o - 2r_h$, therefore, the area per head group is (in Å^2):

$$\underline{a} = \frac{2\,(Z_w/P_w + Z_h/P_h)\,\phi_h \,.\, 10^{24}}{r_h \,.\, N \,.\, M} \qquad (5\text{-}18)$$

Similar expressions can also be found to characterise cubic phases. It is noted, that for the lamellar phase $\underline{a}$ is usually less that 46Å^2 per linear alkyl chain and for the hexagonal phase $\underline{a}$ is in the range 46-70Å^2.

Fig.1 Diagrammatic Representation of a Fixed Stand Polarising Microscope.

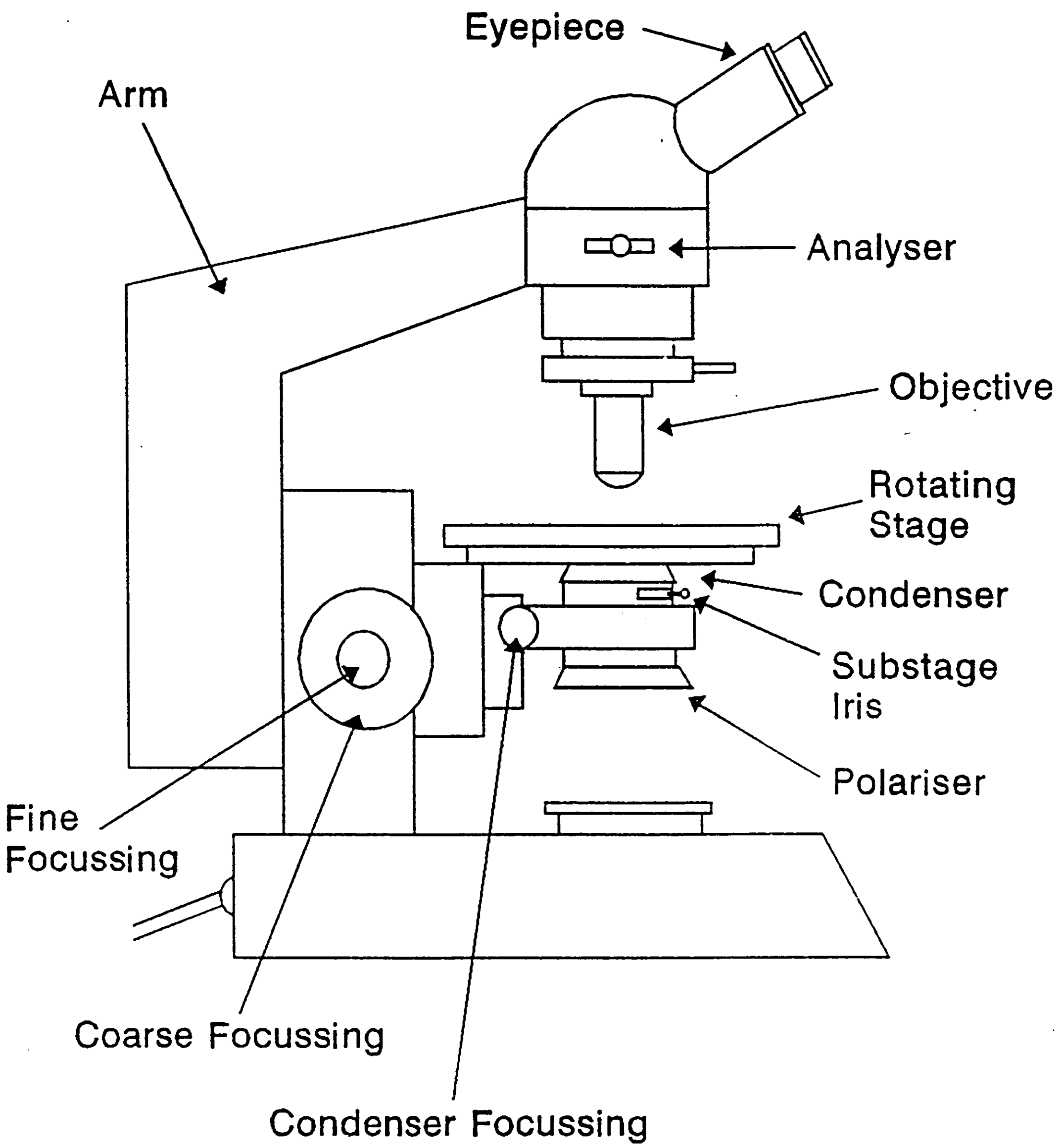


Fig.2 Principal Components of the Polarising Microscope.

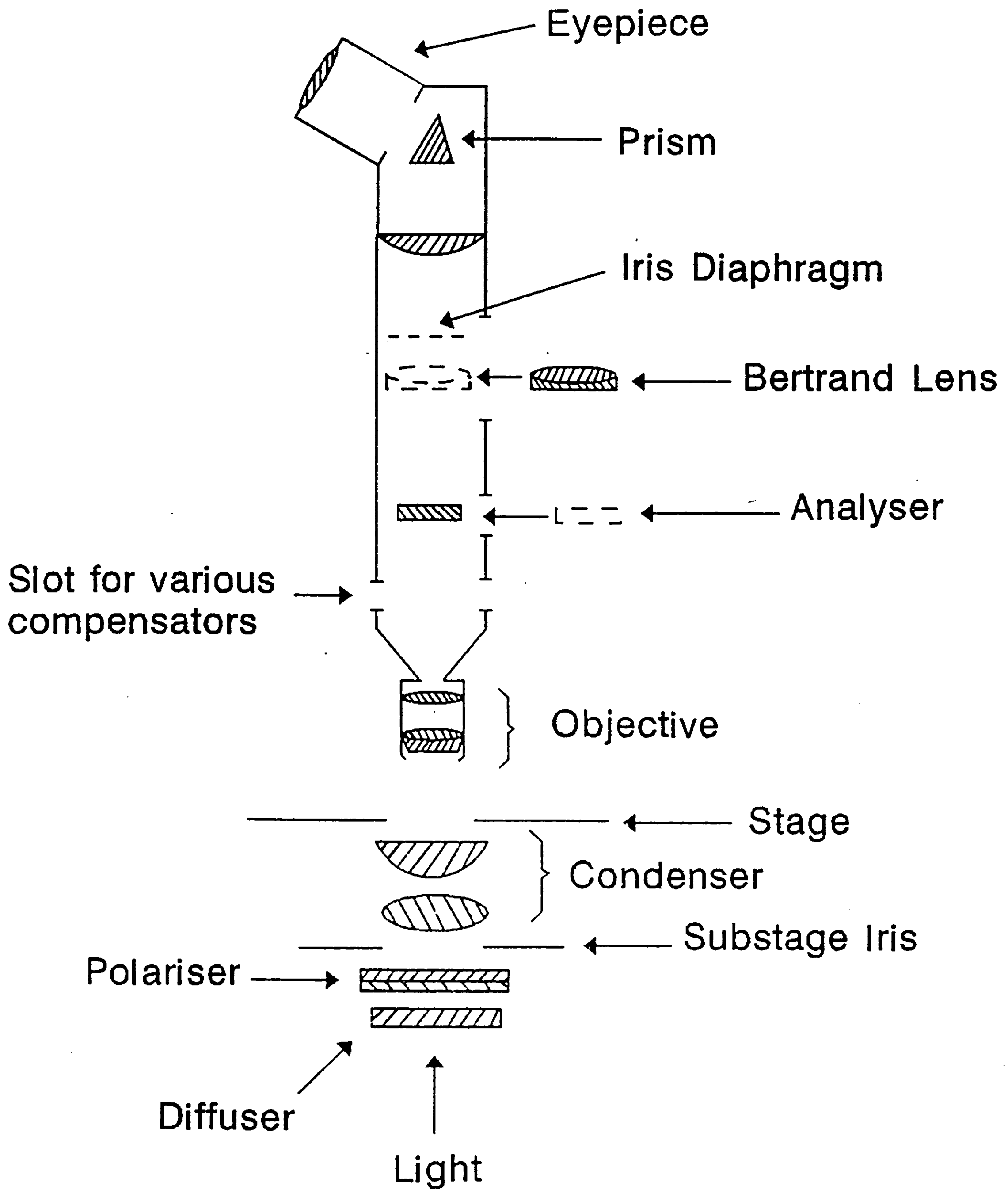


Fig.3 Effect of Light Waves on an Atom Pair.

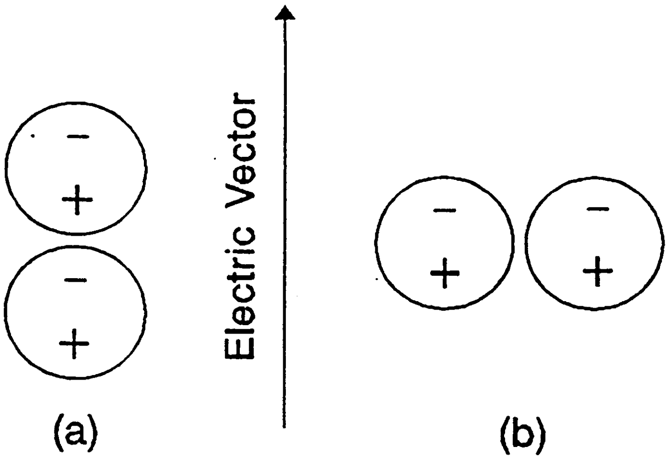
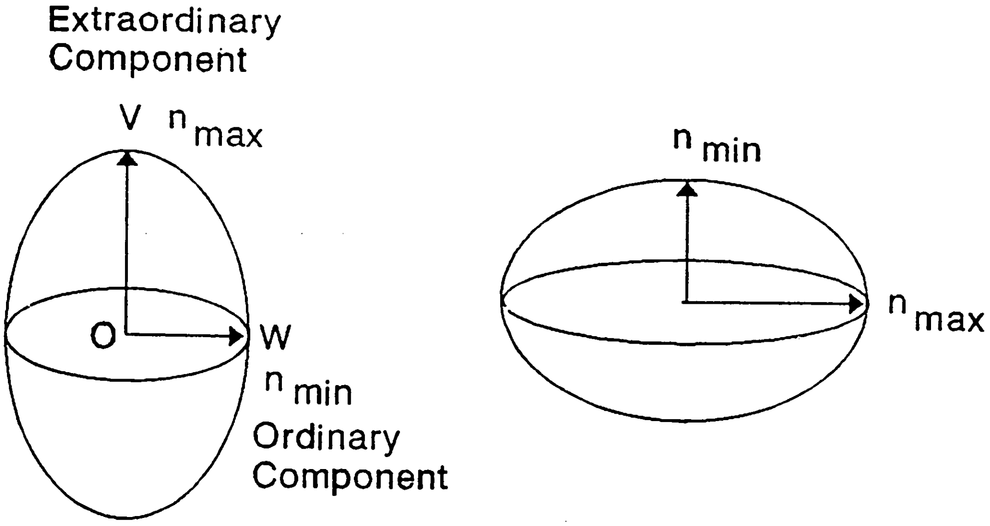


Fig.4

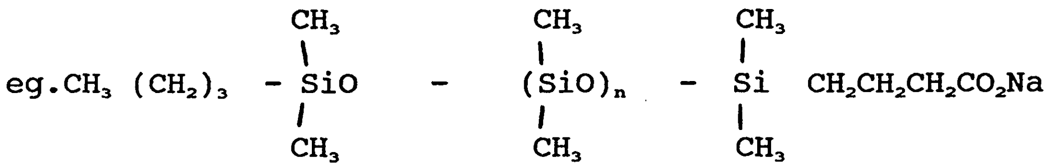
(a)Positive Uniaxial Medium (b) Negative Uniaxial Medium



6. The Phase Behaviour of the Ionic Polymeric Surfactants.

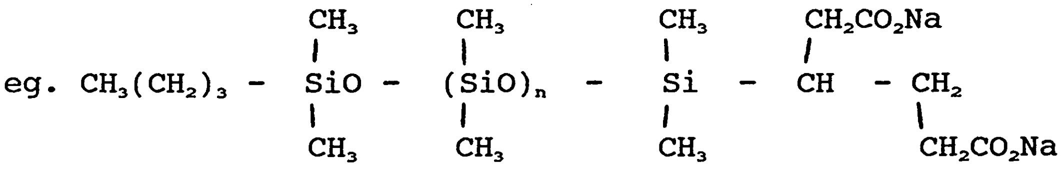
6.1 Introduction

Two sets of novel linear amphiphilic siloxanes were synthesised and isolated in a pure form. The first set consisted of a linear dimethyl siloxane backbone (various chain lengths) with a propyl and a n-butyl alkyl chain attached to opposite ends of the siloxane backbone. The terminal carbon atom of the propyl chain contained a carboxyl moiety bonded to it. The sodium and calcium salts of these carboxylated products were prepared.



eg. $CH_3(CH_2)_3-Si(CH_3)_2O-(Si(CH_3)_2O)_n-Si(CH_3)_2CH_2CH_2CH_2CO_2Na$

The second set of novel compounds consisted of a linear dimethyl siloxane backbone (various chain lengths) with a butyl and a n-butyl alkyl chain attached to opposite ends of the siloxane backbone. Two carbon atoms, of the butyl chain, each formed part of one carboxyl moiety. Only the sodium salts of these carboxylated products were prepared.



eg. $CH_3(CH_2)_3-Si(CH_3)_2O-(Si(CH_3)_2O)_n-Si(CH_3)_2-CH(CH_2CO_2Na)-CH_2CH_2CO_2Na$

As previously discussed, conventional straight chain amphiphiles comprise a polar head group and a hydrophobic, hydrocarbon chain (occasionally a fluorocarbon chain is used (298)). The melting points of these chains rapidly increase with increasing chain length and, therefore, the hydrophobic chains in these conventional materials are crystalline at room temperature and the chain lengths are limited to ≤ ca C_{18} (as longer chain surfactants are insoluble in water). Thermotropic and lyotropic properties of these types of amphiphiles have been studied extensively (299-304).

The use of a polydimethylsiloxane chain (in place of the hydrocarbon chain) enables very long, straight chain amphiphiles to be synthesised because the polydimethylsiloxane chain is flexible and has a low glass transition temperature (ie. $^{-}120^{\circ}C$ (305)). The hydrophobic chain of these amphiphiles may be expected to be non-crystalline in the neat state and, therefore, long chain non-polar moieties may be water soluble at low temperatures.

As many problems arose during the synthesis of these novel amphiphiles only a brief overview of their phase behaviours was possible. The majority of the work concentrated on optical microscope studies, although a small amount of differential scanning calorimetry work was undertaken. This chapter details the phase behaviour studies carried out on the mono- and di-salt amphiphiles, as well as some work carried out on the silanols (ie. $Bu - (Si(CH_3)_2O)_n\ Si(CH_3)_2\ OH$).

6.2 The Phase Behaviour of the Mono-Salt Amphiphiles.

6.2.1 Introduction

As previously discussed, (see Chapter 3.1), Cockett (131) synthesised a mono-salt amphiphile, which had the following structure (it is noted that the calcium salt was also synthesised):

$$\mathrm{Bu - (Si(CH_3)_2O)_n\ Si(CH_3)_2\ (CH_2)_{10}\ CO_2Na} \qquad (6\text{-}1)$$

The hydrophobic backbone of this type of amphiphile consisted of a n-butyl alkyl chain, a polydimethylsiloxane chain (where n = 4-26.5) and an undecyl alkyl chain ie. the backbone contained a large hydrocarbon moiety. It was the aim of this project to reduce the hydrocarbon part of the backbone to a minimum. This was achieved by hydrosilylating benzyl vinylacetate and then making the sodium and calcium salts (see Chapter 3.3.3 for details).

eg. $\mathrm{Bu - (Si(CH_3)_2O)_n\ Si(CH_3)_2\ (CH_2)_3\ COONa}$ (6-2)

where n= 3-21

The optical microscopy and differential scanning calorimetry studies of the two sets of amphiphiles were compiled and the findings are reported in this chapter.

6.2.2 The Sodium Salts

Optical microscopy studies, on Cockett's (131) undecyl containing amphiphile (6-1), suggested that all the homologous amphiphiles existed as ordered fluids, at 0°C. The non-geometric texture and the viscosity of these birefringent fluid phases were characteristic of a hexagonal phase. For all the amphiphiles, this phase was stable up to around 250°C. Where n=10.0, 17.5 and 26.5, the transition occurring at around 250°C resulted in the formation of the low viscosity isotropic liquid. When n=4, the transition occurring at around this temperature resulted in the formation of an additional ordered fluid phase, which was also characteristic of a hexagonal phase. This phase remained up to the transition to the low viscosity isotropic liquid at 312°C.

Optical microscopy studies on the propyl containing amphiphile (6-2) also indicated that the homologous series of amphiphiles existed as ordered fluids, at 0°C. Again the non-geometric texture and the viscosity of the birefringent fluid phases were similar for all the members of the series (n=3, 9, 12 and 21) and were characteristic of a hexagonal phase. On heating, the hexagonal phase was stable up to around 320°C. At this temperature a reduction in the viscosity was observed and charring of the sample occurred. This was believed to be the onset of thermal degradation.

DSC thermograms of the undecyl containing amphiphiles (6-1), between $^{-}170$ - $^{+}350$°C, were characterised by up to five endothermic transitions and a large exothermic transition at around 330°C, which corresponded to the onset of extensive thermal degradation.

Cockett (131) obtained x-ray diffraction data, at various temperatures, on the undecyl containing amphiphiles (6-1) as a source of corroborative evidence. Where the diffraction pattern exhibited more than one reflection, the observed pattern was characteristic of a hexagonal phase and, hence, supported the conclusions drawn from microscopy. Cockett applied the established principles used to explain the phase behaviour of amphiphilic molecules (119) to propose that the hexagonal phase would be made up of a two dimensional hexagonal array of reversed rod micelles (ie. H_2), containing the polar groups in a non-polar continuum. However, this may not be the case in the presence of a polar solvent. Unfortunately, during this study, time did not allow x-ray data to be obtained for the propyl containing amphiphiles (6-2).

The optical microscopy and DSC results obtained for the undecyl (6-1) and the propyl (6-2) containing mesogens are extremely similar and, therefore, it can be concluded that reducing the length of the alkyl chain in the hydrophobic moiety had no significant effect. The greater number of endothermic transitions in the DSC thermograms of 6-1 can be partly explained by the fact that the C_{10} alkyl chain undergoes a two stage melting process, analogous to the initial step-wise melting of conventional monomeric straight chain sodium salts. It is also noted, that below ~120°C the 'liquid like' structure of the polymer would be frozen into a glassy state (306).

The overview of the lyotropic phase behaviour of both sets of amphiphiles (ie.6-1 and 6-2), generated by the use of the penetration technique (as discussed in Chapter 5.2.4), indicated no interaction between the amphiphile and water, between 5 and 100°C. This can be explained by the fact that the molecular structure of the amphiphile is thought to give rise to the formation of reversed rod micelles in the neat state and their resulting packing forms a two dimensional reversed hexagonal phase. Therefore, the siloxane chains constitute the continuous phase. The resulting non-polar continuum, therefore, limits the water solubility of the amphiphiles, and results in the absence of amphiphile-water interactions.

6.2.3 The Calcium Salts

Cockett (131) only studied the undecyl containing amphiphile where n=4. The optical microscope work indicated that the amphiphile was present as a birefringent viscous fluid, at 0°C. This fluid phase had a non-geometric texture and intermediate viscosity indicative of a hexagonal phase. As the amphiphile was heated the birefringence increased and there was a gradual decrease in viscosity. However, there was no phase transition until the transition to the low viscosity isotropic liquid at 450°C.

Optical microscope studies on the propyl containing amphiphile (6-2) indicated that the homologous series of amphiphiles (where n=3,9,12 and 21) existed as ordered fluids at 0°C. The non-geometric texture and intermediate viscosity, observed for all the members of the series, were characteristic of a hexagonal phase. This hexagonal phase was stable up to 420°C. At this temperature the onset of thermal degradation was characterised by the charring of the amphiphile.

A DSC thermogram, of the undecyl containing amphiphile, between $^{-}160$ - $^{+}500$°C, was characterised by three endothermic transitions and a large exothermic transition at 450°C corresponding to thermal degradation.

A DSC thermogram, of the propyl containing amphiphile (n=12), between 25 and 500°C, was characterised by two endothermic transitions and an exothermic transition at 415°C which was thought to be the onset of thermal degradation.

As no x-ray data for any of the calcium salt amphiphiles was available, only tentative observations could be made, based on optical microscopy and DSC results. However, the same conclusions derived for the sodium salt amphiphiles can be drawn for the structure of the calcium salts. That is that the hexagonal phase would be made up of a two dimensional hexagonal array of reversed rod micelles (ie.H_2), containing the polar groups in a non-polar continuum. The results from the sodium and calcium salts of each type of amphiphile (ie. 6-1 and 6-2) are extremely similar, thus indicating the influence of the similar hydrophobic moieties on the phase behaviour of the different amphiphiles.

The lyotropic phase behaviour of both sets of calcium salt amphiphiles (6-1 and 6-2), generated by the use of the penetration technique, again showed no interaction between the amphiphile and water, between 5 and 100°C. This observation was expected and can be explained in the same way as for the sodium salt amphiphiles; ie. the molecular structure of the amphiphile results in the formation of reversed rod micelles in the neat state. Their packing forms a two dimensional reversed hexagonal phase and, therefore, the siloxane chains constitute the continuous phase. The resulting non-polar continuum limits the water solubility of the amphiphiles and results in the absence of amphiphile-water interactions.

6.3 The Phase Behaviour of the Di-Salt Amphiphiles.

6.3.1 Introduction

The lyotropic phase behaviour of the mono-salt amphiphiles showed no interaction between the water and the amphiphiles. By increasing the size of the polar moiety of the amphiphile, it was thought that the head group activity would be increased and the micelle size, shape and properties would be changed. The increase in the head group size was achieved by the use of a di-carboxyl moiety and the synthesis of these amphiphiles is detailed in Chapters 3 and 4. Many problems were encountered during the synthesis of these novel amphiphiles and, therefore, time allowed only for a very brief overview of the phase behaviour of the disodium salt amphiphiles, utilizing optical microscope and DSC techniques.

6.3.2 The Disodium Salts

Optical microscopy studies on the disodium amphiphile (where n=12) indicated that it existed as an ordered fluid at 0°C. No birefringence was observed and the viscous nature was characteristic of a cubic phase. On heating, there was a slight decrease in viscosity but no obvious phase transition occurred until approximately 370°C. At 370°C, charring of the amphiphile was detected and this was thought to be due to the beginning of thermal degradation. This observation was confirmed by differential scanning calorimetry, which showed a large exothermic transition at approximately 350°C.

In the absence of supportive evidence, from x-ray studies, any conclusions drawn can only be very tentative. However, it seems reasonable to suggest that the amphiphile exists in the form of a reversed cubic (V_2) phase.

The overview of the lyotropic phase behaviour of the amphiphile, generated by the penetration technique, indicated a certain amount of interaction between the amphiphile and water, between 20 and 90°C. A small amount of the amphiphile was deposited on a microscope slide and a cover slip was placed over it. A few drops of water was then contacted with the sample, at 20°C, and allowed to stand for 5 minutes. Birefringence was observed when the slide was viewed under the optical microscope. This birefringence was indicative of a lamellar phase as it had a mosaic pattern and flowed when slight pressure was applied to the cover slip. However, the birefringence did not appear as a continuous band but was observed to be patchy. This patchy birefringence was thought to be due to impurities present in the amphiphile. However, the spectral data of the amphiphile did not indicate any impurities and the reason for the patchy nature of the lamellar phase remained unanswered. On heating the amount of birefringence increased, although it was still patchy. This birefringence was stable up to 90°C and was still observed on cooling.

Penetration scans were then generated utilising other solutions. Thus, 15% solutions of octaethyleneglycol mono-n-dodecyl ether ($CH_3(CH_2)_{11}(OCH_2CH_2)_8OH$, a non-ionic surfactant), cetyltrimethylammonium bromide ($CH_3(CH_2)_{15}N(CH_3)_3Br$, a cationic surfactant) and sodium dodecyl sulphate ($C_{12}H_{25}OSO_3Na$, an anionic surfactant) were made up and penetration scans were completed. All 3 penetration scans indicated interaction between the amphiphile and the solutions at 20°C. Once again patchy birefringence was observed at 20°C and on heating to 90°C, the birefringence increased slightly. The mosaic pattern and viscosity were indicative of a lamellar phase.

From these observations, it was concluded that by increasing the size of the polar head group, changes in the thermotropic and lyotropic phase behaviour of the amphiphiles occur. However, the phase behaviours reported here are by no means comprehensive and to achieve the overall thermotropic and lyotropic behaviour of these novel amphiphiles, more thorough optical microscopy and differential scanning calorimetry studies, as well as x-ray diffraction and nuclear magnetic resonance spectroscopy studies, would have to be compiled and reported.

6.4 The Phase Behaviour of the Silanols

The silanols (see 6-3) comprise a hydrophobic backbone and a polar head group and therefore, their phase behaviours were briefly investigated.

eg. $Bu - (Si(CH_3)_2O)_n\ Si(CH_3)_2\ OH$ (6-3)

The silanols were prepared via the anionic polymerisation of hexamethylcyclotrisiloxane, and the values of n synthesised were 3,9,12 and 21.

The overview of the lyotropic phase behaviour of the amphiphile, generated by the penetration technique, indicated no interaction between the amphiphile and water, between 20 and 100°C. Penetration scans were then completed on all the homologous silanols using a 30% solution of hexadecyltrimethylammonium chloride ($CH_3(CH_2)_{15}N(CH_3)_3Cl$, a cationic surfactant). However, again no interactions were observed between 20 and 100°C. Since no interactions were observed, further studies were not undertaken.

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8. Appendix - Synergism in Mixtures of Two Surfactants.

8.1 Introduction.

If, when two surfactants are mixed, the properties of the mixture are better than those attainable with the individual components by themselves, synergism is said to occur. For example, a long-chain amine oxide is often mixed with an anionic surfactant as the foaming properties of the mixture are better than those of either surfactant by itself.

Mixtures of surfactants, rather than individual surfactants, are used in most practical applications. This is sometimes unavoidable as some commercial surfactants, even when designated by the name of an individual surfactant (eg. sodium lauryl sulphate, $CH_3(CH_2)_{11}OSO_3Na$), are mixtures of surface-active materials as a result of the nonhomogenous raw materials used and/or the presence of unreacted raw materials and manufactured by-products. However, in other cases, surfactants are purposely mixed to improve the properties of the final product.

The two fundamental properties of surfactants are monolayer formation at interfaces and micelle formation in solution, therefore, for surfactant mixtures, the characteristic phenomena are mixed monolayer formation at interfaces and mixed micelle formation in solution. The molecular interaction of these latter phenomena can be evaluated using a number of equations derived by Rubingh (1) and Rosen (2). The relations between synergism in the fundamental properties of mixed monolayer formation at an interface or mixed micelle formation in solutions and synergism in various practical applications of surfactants is still a relatively unexplored area. Some recent studies (3-6) have probed this area, but much remains to be known.

8.2 Synergism and Docosyl Trimethyl Ammonium Chloride (C_{22} TACl).

The overview of the lyotropic phase behaviour of docosyl trimethyl ammonium chloride ($CH_3(CH_2)_{21}N(CH_3)_3Cl$), generated by the use of a penetration technique, indicated an interaction between the amphiphile and water at 30.7°C. At 30.7°C, a birefringent band, between the dilute micellar solution and the solid, neat surfactant, was observed. This birefringence was indicative of a hexagonal phase, as it did not flow much under pressure, contained distorted air bubbles and had a non-geometric texture. The hexagonal phase melted at approximately 55°C and on cooling reappeared at approximately 53°C.

The penetration technique only indicated which phases were formed; it was not specific with regard to the compositions at the mesophase boundaries. Therefore, different samples of known composition were made up and studied as a function of temperature (see Chapter 8.3.1

for experimental details); Table 1 shows the results from these experiments.

At compositions less than 21% (w/v) of C_{22} TACl no hexagonal phase is observed. However, at 22% (w/v) composition the characteristic viscosity and texture of a hexagonal phase is detected. It has been the aim of this section to add another surfactant to the C_{22} TACl solutions in an attempt to achieve a hexagonal phase at lower concentrations than 22% (w/v).

The first set of co-surfactants added were long chain alcohols. The mole ratio of C_{22}TACl to the long chain alcohol was kept constant so as to compare the synergic effect of each. The long chain alcohols added were oleyl alcohol ($CH_3(CH_2)_7CH=CH(CH_2)_8OH$), 1-tetradecanol ($CH_3(CH_2)_{13}OH$) and 1-octanol ($CH_3(CH_2)_7OH$) (see Chapter 8.3.1 for experimental details). The results from the polarising microscope work are given in Tables 2-4.

These tables indicate synergism occurring on the addition of each of the alcohols. The lowest composition of C_{22}TACl, that gives a hexagonal phase, for each of the alcohols was 14.0% (for oleyl alcohol), 17.0% (for 1-octanol) and 16.0% (for 1-tetradecanol). Therefore, these results seem to indicate that the longer the alkyl chain the greater the synergic effect.

Since oleyl alcohol had the greatest synergic effect, samples containing a larger mole ratio of oleyl alcohol were made up in an attempt to obtain a hexagonal phase from a solution of C_{22}TACl of composition lower than 14.0% (w/v). The results from these tests (Table 5) indicated that the lowest composition, that gave a hexagonal phase, was in fact 14.0% (w/v).

A non-ionic surfactant, namely hexaethyleneglycol mono n-hexadecyl ether (CH_3 $(CH_2)_{15}$ $(OCH_2CH_2)_6$ OH) was then used as a co-surfactant (the results are outlined in Table 6). The lowest composition that a hexagonal phase formed was 12.0% (w/v) and therefore the addition of this non-ionic had a greater synergic effect on C_{22}TACl than the addition of oleyl alcohol.

Finally, the addition of inorganic salts to 20.0%, 10% and 5% (w/v) solutions of C_{22}TACl were investigated. On addition of sodium chloride and sodium sulphate to separate 20%(w/v) solutions of C_{22}TACl, gel phases were observed. A gel phase was also observed when sodium chloride was added to a 10% (w/v) solution of C_{22}TACl. However, no liquid crystalline phase was observed on addition of sodium chloride to a 5%(w/v) solution of C_{22}TACl.

8.3 Experimental

8.3.1 Sample Preparation

The accurately weighed sample of C_{22}TACl was placed in a sample vial and 1ml (pipetted) of distilled water was added. The sample was then heated in an oven to 40°C, with intermittent shaking, to form a homogenous solution. A drop of the homogenous solution, at 40°C, was then placed on a pre-heated microscope slide and a coverslip placed over it. The sample was then viewed at 40°C, under a polarising microscope. Any phases that were observed were noted and their melting points obtained.

When co-surfactant was required, it was added to the C_{22}TACl solution prior to heating in the oven.

Table 1. Bulk Samples of Docosyl Trimethyl Ammonium Chloride.

Percentage composition of C_{22}TACl in water	Hexagonal Formed	melts/°C	Reappears/ °C
8.0	NO	-	-
10.0	NO	-	-
15.0	NO	-	-
17.0	NO	-	-
18.5	NO	-	-
19.0	NO	-	-
20.0	NO	-	-
21.0	NO	-	-
22.0	YES	53-55	50-48
24.0	YES	54-56	52-50
25.0	YES	55-56	51-50

Table 2. Addition of Oleyl Alcohol

Percentage composition of C_{22}TACl in water	Mole ratio of C_{22}TACl to Oleyl Alcohol	Hexagonal formed	melts/°C
17.0	4:1	YES	57
15.2	4:1	YES	53
14.0	4:1	YES	50
12.9	4:1	NO	-
12.0	4:1	NO	-

Table 3. Addition of 1-Tetradecanol

Percentage composition of C_{22}TACl in water	Mole ratio of C_{22}TACl to 1-tetradecanol	Hexagonal formed	melts/°C
20.0	4:1	YES	53
17.0	4:1	YES	51
16.0	4:1	YES	50
15.0	4:1	NO	-
14.0	4:1	NO	-

Table 4. Addition of 1-Octanol

Percentage composition of C_{22}TACl in water	Mole ratio of C_{22}TACl to 1-Octanol	Hexagonal formed	melts/°C
20.0	4:1	YES	51
17.0	4:1	YES	48
16.0	4:1	NO	-
15.0	4:1	NO	-

Table 5 Addition of a Greater Amount of Oleyl Alcohol

Percentage composition of C_{22}TACl in water	Mole ratio of C_{22}TACl to Oleyl Alcohol	Hexagonal formed	melts/°C
14.0	4:1	YES	50
14.0	3:1	YES	51
14.0	2:1	YES	51
13.0	4:1	NO	-
13.0	3:1	NO	-
13.0	2:1	NO	-
12.0	2:1	NO	-

Table 6. Addition of Hexaethyleneglycol mono n-Hexadecyl Ether ($C_{16}EO_6$)

Percentage composition of C_{22}TACl in water	Mole ratio of C_{22}TACl to $C_{16}EO_6$	Hexagonal formed	melts/°C
10.0	4:1	NO	-
10.0	3:1	NO	-
10.0	2:1	NO	-
12.0	4:1	NO	-
12.0	3:1	YES	46
12.0	2:1	YES	46
15.0	4:1	YES	48

8.4 References

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Research Study Programme

As part of this project the author has attended the following lecture courses at Sheffield University:

(1) Liquid Crystal Group, Autumn 1990 (a series of 8 lectures).

(2) Liquid Crystal Group, Spring 1991 (a series of 8 lectures).

(3) Polymers and Structured Fluids, Spring 1991 (a series of 4 lectures).

The author has attended research colloquia given by internal and external speakers at Sheffield Hallam University and Sheffield University.

The author has also attended the following seminars:

(1) British Liquid Crystal 2 day seminar. Leeds University, November 1989.

(2) Polymer Group 1 day Seminar. Sheffield Hallam University, January 1990.

(3) R.S.C. Perkin Division. East Midlands Regional Meeting, Nottingham University, March 1991.

Finally, the author attended the S.E.R.C. Graduate School at Oxford Polytechnic (August 1991) and presented a poster at the 9th International Symposium on Surfactants in Solution at Varna, Bulgaria (June 1992).