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*Calcium ion-selective electrodes with covalently-bound sensor groups.*

ELLIS, Andrew T.

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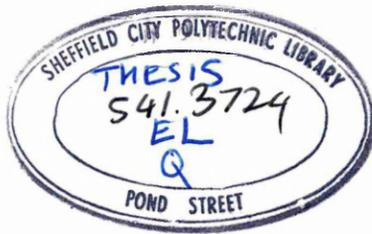
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of  
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### Abstract.

A review of the development of ion selective electrodes (ISE), with particular emphasis on calcium ISE, is presented. The utility, in terms of an increased electrode operational lifetime and opportunities for the enhancement of selectivity and sensitivity, of a calcium ISE membrane with a covalently-bound ion-exchange sensor group is indicated. The production of such a covalently-bound sensor (CBS) membrane by the crosslinking of styrene-b-butadiene-b-styrene triblock elastomer with triallyl phosphate (TAP) using a free radical initiated copolymerisation is described. Various methods of forming such ion-exchange membranes were investigated. The resulting membranes were hydrolysed in methanolic KOH to yield covalently-bound dialkylphosphate exchange sites. These membranes were then used to fabricate a robust calcium ISE. The response range, selectivity and general analytical utility of such electrodes are evaluated and the electrodes used in the determination of water hardness and of calcium in coking plant effluent. The modification of the ion-exchange site by using either trioctyl phosphate, tri(10-undecenyl) phosphate or diallyl phenylphosphonate as cross-linking agent is described and the subsequent effects on electrode performance are discussed. A method enabling the elimination of the hydrolysis step during membrane production resulting in a second pathway to the production of a covalently-bound

dialkylphosphate sensor is also described. The use of covalently-bound mediator materials in the electrode membrane is investigated and their effect on membrane performance discussed. The incorporation of an entangled solvent-mediator in conjunction with a dialkylphosphate sensor, which yielded a calcium ISE with good selectivity for  $\text{Ca}^{2+}$  in the presence of  $\text{Mg}^{2+}$  and  $\text{Na}^+$  ions, is described. Results from various mechanistic studies including radiotracer and electron microprobe techniques are presented. Possible mechanisms for the response and selectivity of CBS electrodes are discussed on the basis of these studies.

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CHAPTER 1

THE DEVELOPMENT OF CALCIUM  
ION SELECTIVE ELECTRODES

## 1.1 The Development of Ion Selective Electrodes.

The late 1960's and early 1970's saw a great upsurge of interest and rapid development in the field of ion selective electrodes (ISE). The subsequent consolidation of their position in analytical chemistry as reliable and versatile analytical tools which occurred during the last decade has made it possible to put forward various criteria which might be applied to an ideal ISE.

### 1.1.1 Electrode response.

When an ion-selective electrode in conjunction with a suitable reference electrode is placed in a solution containing an ion,  $i$ , to which the ISE responds, it is desirable that the potential developed is related to the activity of ion  $i$  in the bathing solution by the Nernst equation:-

$$E = E^0 \pm \frac{2.303RT}{z_i F} \log_{10} a_i.$$

In particular, the slope of the  $E$  vs.  $\log_{10} a_i$  plot should be e.g. for a divalent cation, + 29.6 mV per decade change in ion activity at 25°C.

### 1.1.2 Electrode selectivity.

Few, if any, ion selective electrodes are perfectly selective for a single ion in the presence of any other ion. Consequently, in mixed ionic solution, the response of an ISE to the primary ion,  $i$ , is modified in the presence of an interfering ion,  $j$ . Thus, the Nernst relationship must be expanded to

incorporate the contribution of this response to the interferent ion in addition to the response to the primary ion. This results in the general equation:

$$E = E^{\circ} + \frac{2.303RT}{z_i F} \log_{10} \left[ a_i + k_{ij}^{\text{pot}} \cdot a_j^{n_i/n_j} \right]$$

in which the potentiometric selectivity coefficient,  $k_{ij}^{\text{pot}}$  is an evaluation of the degree of selectivity of the electrode for the primary ion, i over the interfering ion, j. In general, values of  $k^{\text{pot}} < 1$  indicate selectivity for the primary ion and values  $> 1$  indicate a greater response to the interferent ion than to the primary ion.

### 1.1.3 Analytical Performance.

Ion selective electrodes should be simple to set up, calibrate and use and should be capable of giving response times in the order of seconds or, failing that, a few minutes rather than hours. In use, the precision and day to day drift should be conducive to meaningful analyses and might be expected to be of the order of 1 mV in each case. The activity range over which an ISE responds in a Nernstian manner should be several orders of magnitude and is typically  $10^{-4}$  to  $10^{-1}$  Molar. The lower limit of detection, where the deviation from Nernstian behaviour is great, depends upon the type of electrode, but will usually lie in the sub-ppm range i.e. around  $10^{-5}$  M.

### 1.1.4 Physical Characteristics.

Primarily, a useful ion-selective electrode should be sufficiently robust to allow field usage and should be able to function in physically or chemically hostile environments such

as might be found in chemical plant monitoring. The lifetime of an ISE, both in use and 'on the shelf', should be long, preferably lasting for a period of months rather than days.

Additionally, it would be useful for the electrode to be commercially available and usable without modification to existing equipment or to be simply constructed in the laboratory.

On the basis of these criteria it is possible to trace the development of one particular ion selective electrode - that for calcium ion. From its rudimentary beginnings, the calcium ISE has become a reliable and widely applied analytical sensor which, at present, meets many, but not all, of the above 'ideal' criteria.

## 1.2 The Development of Calcium Ion Selective Electrodes.

### 1.2.1 Introduction.

The development of calcium ion selective electrodes (ISE) has been closely paralleled throughout its history by the development of interest in the determination of ionised calcium in biological fluids. Initially, at the turn of the century, was the discovery of the glass electrode<sup>1,2</sup> selective for hydrogen ion and during the same era results<sup>3</sup> indicating the presence of two different forms of calcium (diffusible and non-diffusible) in serum. However, the lack of analytical methods for the determination of the state of calcium in biological fluids made interpretation of these diffusible and non-diffusible forms of calcium very difficult and somewhat speculative.

In the 1930's reviewers<sup>4,5</sup> generally supported the view that 'the diffusible calcium in the body fluids is partly ionised

and partly bound to some citrate-like substance as yet unidentified'. McLean described a method<sup>6</sup> for the determination of ionised calcium using 'the amplitude of contraction of the ventricle of the isolated heart of the frog' which was then used to investigate calcium complexation<sup>7</sup> and the amount and state of calcium in the blood<sup>8,9</sup>, the results of which are summarised in Table 1-1.

Table 1-1

The amount and state of calcium in the blood

Total Calcium	10 mg./100cc.
Non diffusible calcium (Ca-Prot) Calcium bound to protein	5
Ionised calcium (Ca <sup>2+</sup> )	4.5
Diffusible, but not ionised calcium (Ca-X)	0.5

Data taken from Ref.9.

From these results it was suggested that (Ca<sup>2+</sup>) could be calculated from (Total Ca) - (Prot) and that it was the ionised calcium concentration in the blood which was the physiologically significant factor. Despite these important findings, the frog heart technique had obvious and very severe limitations and was only adopted for this single study. In the meantime methods for the potentiometric determination of calcium ion had followed on from the interest generated by the glass pH electrode.

### 1.2.2 Early electrode methods for calcium.

The first type of electrode to be used for calcium determination was an amalgam electrode<sup>10</sup> which was an electrode of the third kind. This system consisted of calcium oxalate and either lead or silver oxalate amalgam. The calcium salt being slightly the more soluble and so the limit of detection (LOD) was limited to  $10^{-4}$  M calcium. Using this type of electrode, Corten and Estermann<sup>11</sup> obtained a Nernstian response over the range  $10^{-1}$  to  $10^{-3}$  M Ca and achieved the possible range for the determination of calcium in serum and blood.

In later studies with  $\text{Hg}/\text{Hg}_2\text{WO}_4 - \text{CaWO}_4 - \text{Ca}^{2+}$  and  $\text{Hg}/\text{Hg}_2\text{Ox} - \text{CaOx} - \text{Ca}^{2+}$  electrodes<sup>12</sup> the calibration was extended to  $10^{-5}$  M  $\text{Ca}^{2+}$  but interference from  $\text{Na}^+$  showed an increase in the LOD, in contrast to later work<sup>13</sup> using a  $\text{PbOx} - \text{CaOx}$  electrode, which reported no significant interference from  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{Mg}^{2+}$ . Except for indicating the possibility of using potentiometric methods for calcium determination, the findings of these studies were limited but the techniques adopted were seen to be much more convenient than the frog's heart method.

### 1.2.3 Crystal membrane calcium electrodes.

The use of thin crystals of naturally occurring fluorite ( $\text{CaF}_2$ ) as membranes for the potentiometric determination of calcium in pure aqueous solutions and in milk was first described by Tendeloo<sup>14</sup>. These results indicated a sub-Nernstian response for this electrode down to an LOD of  $10^{-4}$  M which was governed by the solubility of  $\text{CaF}_2$ . However, it was suggested<sup>15</sup> that these electrodes were merely 'crack' electrodes and although further work<sup>16,17</sup> refuted these claims, the lack of selectivity and poor LOD shown

by these electrodes were major drawbacks.

Crystalline materials other than fluorite have been used, such as the zeolite apophyllite<sup>18</sup>, which yielded a cationic electrode with little or no selectivity and with a sub-Nernstian slope. The latter observation was explained in terms of anion or water transport within the membrane. Much more recently<sup>19</sup>, a europium-doped fluorite membrane electrode has been prepared which, by judicious choice of internal filling solution, has been found to give a Nernstian response to  $\text{Ca}^{2+}$  with selectivity over many cations and the use of  $\text{CaF}_2$  powder in a polystyrene matrix<sup>20</sup> has been reported to give a good Ca ISE.

#### 1.2.4 Calcium electrodes with paraffin matrix or other solid ion exchange membranes.

During the 1950's Tendeloo carried out a series of studies using membranes produced from pure paraffin containing calcium oxalate and a non-ionic detergent.<sup>21</sup> The selectivity of electrodes incorporating these membranes was studied<sup>22,23</sup>, and found to be erratic but such electrodes were used in the study of the effect of gelatin on calcium concentration<sup>29</sup> and calcium in human serum<sup>25</sup>. However, the response of these electrodes<sup>26</sup> was generally poor, sometimes anionic and always sub-Nernstian for  $\text{Ca}^{2+}$  and further studies<sup>27,28</sup> showed this type of membrane to be permeable to both anions and cations, to have only a very small number of charged ion-exchange sites and to be non selective. It was suggested that any selectivity observed perhaps was due to readings being taken before a true equilibrium potential had been attained. It has also been shown<sup>28</sup> that paraffin membranes act as insulators unless

they are cracked whereupon they give a non-selective response.

Various ion-exchange materials both natural<sup>29,30</sup> and synthetic<sup>31,32,33</sup> have been used in membrane electrodes, either alone or incorporated into a polymer binder (matrix). Much of this work has been reviewed<sup>34,35</sup> and it has been concluded<sup>36</sup> that this type of membrane is only permselective for ion type, showing little or no selectivity for any individual ion, hence an electrode produced using calcium oxalate in a polystyrene matrix has been used for end point determination in the titration of (Ca+Mg) with EDTA.<sup>37</sup>

Other membranes have been prepared such as a multilayer membrane<sup>38</sup> for  $\text{Ca}^{2+}$  employing a calcium stearate monolayer formed between the edges of a precisely cracked glass slide. Although used to determine calcium activities in mixed electrolyte solutions<sup>39</sup> successfully, this type of electrode has not been widely used due to the difficulty of preparation and the complex design.

#### 1.2.5 Glass electrodes for calcium.<sup>40</sup>

An early attempt<sup>41</sup> to produce a glass electrode for a Ca ISE met with little success, but as glass electrodes for monovalent cations other than  $\text{H}^+$  became available, further attempts to produce glass electrodes for divalent cations were made. Investigations of a number of natural glasses<sup>42</sup> and of a phosphate glass made from radioactive waste materials<sup>43</sup> yielded electrodes with divalent over monovalent selectivity, but with little selectivity among divalent cations. Despite the observation<sup>44</sup> of a transient, near-Nernstian response of a glass electrode to  $\text{Ca}^{2+}$  little further development has occurred. It has been suggested<sup>45</sup>

TABLE 1-2. The Development of liquid ion exchange membrane electrodes for calcium.

Workers(date)	Refs.	Sensor*	Solvent mediator*	Slope(mV.pCa <sup>-1</sup> Range(M))	Selectivity, K <sub>CaM</sub> <sup>Pot</sup>	Remarks
Bonner & Lunney (1966)	46	Ca(DNMS) <sub>2</sub>	nitrobenzene o-dichlorobenzene (1:1)	Nernstian 3x10 <sup>-3</sup> -3x10 <sup>-1</sup>	Ca <sup>2+</sup> > Na <sup>+</sup> > NH <sub>4</sub> <sup>+</sup>	Poor range, flow through membrane
Ross (1966/67)	47 48	Ca(DDP) <sub>2</sub>	DOPP	+29 10 <sup>-5</sup> -10 <sup>-1</sup>	Mg <sup>2+</sup> =0.014, Ba <sup>2+</sup> =0.01 Na <sup>+</sup> =K <sup>+</sup> =NH <sub>4</sub> <sup>+</sup> =10 <sup>-4</sup>	Orion 92-20, H <sup>+</sup> and Zn <sup>2+</sup> interfere
Shatkay (1967)	49	Ca(oxalate)	Non ionic detergent + paraffin	-15 to -20 10 <sup>-3</sup> - 10 <sup>-1</sup>	Porous, non-perm-selective. Not selective	Tendaloo type Paraffin support. Long equilibration.
Bloch & Shatkay (1967)	49 50 51	TTA	TBP	+27/28 10 <sup>-4</sup> -10 <sup>-1</sup>	Comparable to Orion except Ba <sup>2+</sup> interferes strongly	PVC membrane, response time slows with interferent.
Coring (1968, passed)	57	Ca(dZEPH) <sub>2</sub>	DOPP n-decanol	+28 +25	Good selectivity over Mg <sup>2+</sup> , Na <sup>+</sup> Poorer selectivity than DOPP	Use of polymer support. Show (Mediator) >
Schultz (1968)	58	HDOP	none	+29 10 <sup>-4</sup> -10 <sup>-1</sup>	Mg=0.34, Ba=0.94, Na <sup>+</sup> =0.039, K <sup>+</sup> =0.034	Poor selectivity - no mediator. Collision matrix.
Harrell (1969)	60	Ca(DNMS) <sub>2</sub>	Nujol	+17.8 10 <sup>-3</sup> -10 <sup>0</sup>	Much less selective than Orion.	Millipore support. Long response time. Sub-Nernstian slope due to H <sub>2</sub> O transport.
Moody & Thomas (1970)	72	Ca(DDP) <sub>2</sub>	DOPP	+29 5x10 <sup>-5</sup> -10 <sup>-1</sup>	Mg 0.036, Ba=10 <sup>-2</sup> As Orion. Na <sup>+</sup> , K <sup>+</sup> =10 <sup>-5</sup>	PVC Matrix. Extended lifetime.
* DNMS - dinonylnaphthalene sulphonate						
DDP - didecylphosphoric acid						
DDPP - dioctylphenylphosphonate						
TTA - Thenoyltrifluoroacetone						

that the major restriction when designing ISE for ions other than Group Ia and Ib cations using solid ion exchangers, is the tendency for decreases in mobility to offset any increases in ion exchange affinity for multivalent (or large) cations in solids'. It may have been for this reason that attention turned away from solids to the liquid ion exchanger electrodes which not only offered good multivalent cation affinity but allowed mobility of the exchanger sites within the membrane, in the hope of producing a viable Ca ISE.

#### 1.2.6 Liquid ion exchange membrane electrodes.

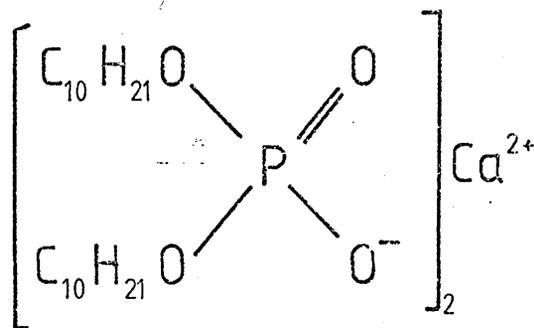
This type of electrode utilizes a membrane formed from an organic solution of a water-insoluble ionogen. Many such systems are known (Table 1-2) and the use of calcium dinonylnaphthalenesulphonate  $\text{Ca}(\text{DNSS})_2$  in 1:1, nitrobenzene:ortho-dichlorobenzene was first suggested<sup>46</sup> for use in a calcium ISE. Despite showing selectivity over monovalent cations, this system exhibited low slopes ( $< 29 \text{ mVpCa}^{-1}$ ) with a narrow range ( $3 \times 10^{-3} - 3 \times 10^{-1} \text{ M Ca}^{2+}$ ) and the production of a continually-replenished membrane required rather complex apparatus.

It was in 1966 with the publication of results for  $\text{Ca}^{2+}$  determination in sea water<sup>47</sup> using a new and highly selective Ca ISE, that a major advance was made. This electrode was described by Ross<sup>48</sup> and was based upon a liquid ion-exchanger retained by a dialysis membrane. The exchanger was a solution of calcium didecylphosphate,  $\text{Ca}(\text{DDP})_2$  in dioctylphenylphosphonate, (DOPP) (Fig. 1-1), and the resulting electrode gave a theoretical response

Figure 1-1

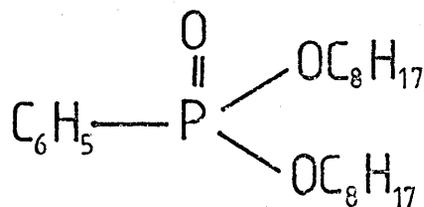
Ross liquid ion-exchanger for calcium

Sensor



Calcium didecyl phosphate

Solvent-mediator



Diocetylphenylphosphonate

over the range  $10^{-4}$  -  $10^{-1}$  M  $\text{Ca}^{2+}$  with selectivity over monovalent, ( $k_{\text{CaNa}}^{\text{pot}} = 10^{-4}$ ) and divalent, ( $k_{\text{CaMg}}^{\text{pot}} = 0.014$ ) cations.

Around the same time, Shatkey and co-workers<sup>49</sup> repeated the work of Tendeloo<sup>21-26</sup> using paraffin membranes containing calcium oxalate and found these electrodes to be non-permselective and unselective for calcium suggesting that any selectivity may have been due to mobility differences within the membrane phase and to the long equilibrium time. However, using a membrane composed of poly(vinyl chloride), (PVC); tributylphosphate and thenoyltrifluoroacetone (TTA)<sup>49,50</sup> an electrode in many ways comparable with Ross's electrode was produced<sup>51</sup>, with good selectivity over  $\text{Mg}^{2+}$  and  $\text{Na}^+$ , but with poorer selectivity over  $\text{Ba}^{2+}$  and a longer response time. Although further studies have been reported<sup>52</sup> and patents granted<sup>53,54,55</sup> using a fabric coated with the TTA exchanger or with the exchanger in carbon paste<sup>56</sup>, interest in this type of electrode seems to have waned in favour of systems employing an organophosphorus ion exchanger.

Using an exchanger similar to that of Ross, Corning obtained a patent<sup>57</sup> in 1968 in which was described an electrode system for calcium incorporating calcium bis (di-2-ethylhexyl phosphate) either in n-decanol or DOPP. This patent indicated many facets of this type of electrode, in particular:

- a) selectivity may be influenced by altering the solvent mediator;
- b) the mediator: sensor ratio should exceed 4:1 and be preferably 8:1 or 10:1.
- c) the exchanger may be supported in a polymeric film.

Similarly, the importance of the solvent mediator and the possibility of using collodion as a matrix/support was demonstrated<sup>58</sup>, using calcium dioctylphosphate sensor with no solvent mediator, where selectivities were much poorer (Table 1-2) than for other membranes incorporating both a dialkylphosphate sensor and a solvent mediator (e.g. DOPP). Despite the lack of selectivity this electrode was applied successfully<sup>59</sup> and had the advantages of a much simpler 'solid' exchanger design and a fast response time.

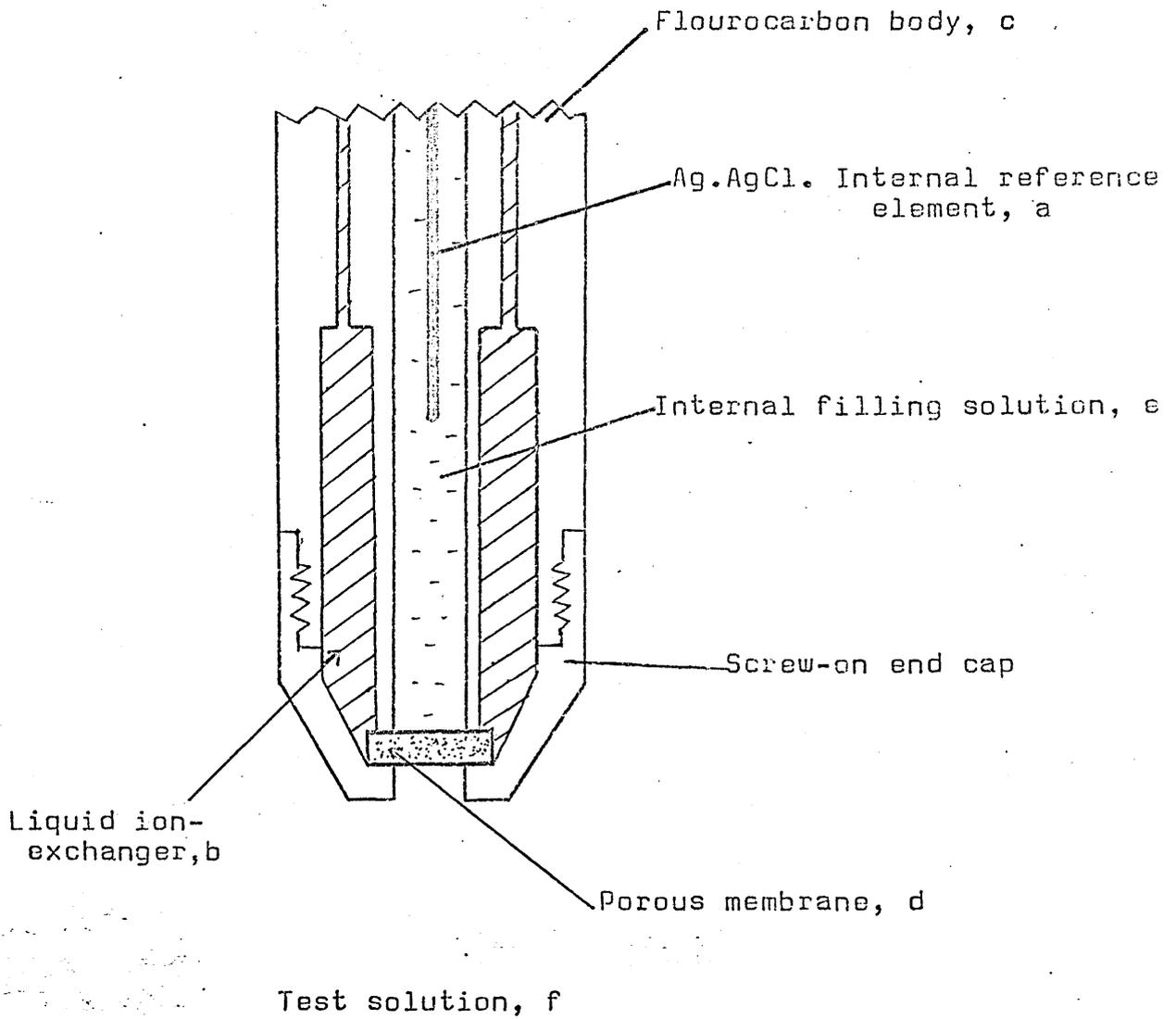
A further attempt<sup>60</sup> to devise a Ca ISE using  $\text{Ca}(\text{DNNS})_2$  in Nujol was largely unsuccessful, resulting in an electrode with a low slope ( $+ 17.8 \text{ mV.pCa}^{-1}$ ), poor selectivity and a long response time. The sub-Nernstian slope was attributed to transport of water molecules within the liquid membrane and the DNNS system has been abandoned as a calcium sensor in favour of the much more selective dialkylphosphate/DOPP systems.

#### 1.2.7. The Ross electrode<sup>48</sup>.

This electrode represented a landmark in the development of calcium ISE as it enabled, for the first time, the direct determination of calcium ion activity in biological and other complex media<sup>47</sup>. Although marketed commercially as the Orion 92-20, this electrode suffered from drawbacks - many of which arose from the rather complex design of the electrode (Figure 1-2). The complexity of this design arose from the need to maintain three solutions, the internal reference solution, the ion exchanger and the test solution, in electrochemical contact whilst preventing their mutual mixing. Thus, the internal reference element (a), and the liquid ion exchanger (b), are contained in concentric

FIGURE 1-2.

The Design of the Ross calcium electrode.



reservoirs in the fluourocarbon barrel (c), whence the exchanger liquid may wick into a microporous filter disc (d), so placing a thin film of the exchanger between the internal reference (e) and the test (f) solutions. In practice the electrode was difficult to handle, bulky and often retained a bubble of air next to the membrane. Chemically, the limit of detection (LOD) and the electrode lifetime were limited by the migration of ion exchanger (a calcium salt) from the membrane into the test solution. The electrode also suffered from severe  $Zn^{2+}$  and  $H^+$  interference, showing characteristic dips<sup>61</sup> (e.g. see Fig.1-3) in the potential-pH curves and from less common interferences, such as cyclohexylammonium ion<sup>62</sup> and certain surfactants<sup>63</sup>. Despite these limitations, this electrode has been used for many applications, in potentiometric titrations<sup>64,65,66</sup>, biomedical research<sup>67,68</sup> and for studies of calcium ion activity in concentrated solution.<sup>69,70,71</sup>

A logical, but very important development in calcium ISE came in 1970<sup>72</sup> with the attempted combination of the best features from the Orion system (selectivity, commercial acceptability) with those from the 'solid' membrane electrodes<sup>49,57,58</sup> (robustness, speed of response and simplicity). This was achieved by the incorporation of either the Orion liquid ion exchanger or purified components of this (calcium bis (didecylphosphate) + DOPP) into a poly(vinyl chloride), (PVC), matrix membrane. Electrodes made from such a membrane showed response characteristics very similar to Ross's electrode<sup>48</sup> with added advantages in terms of increased robustness, simplicity and particularly in having a significantly increased lifetime.

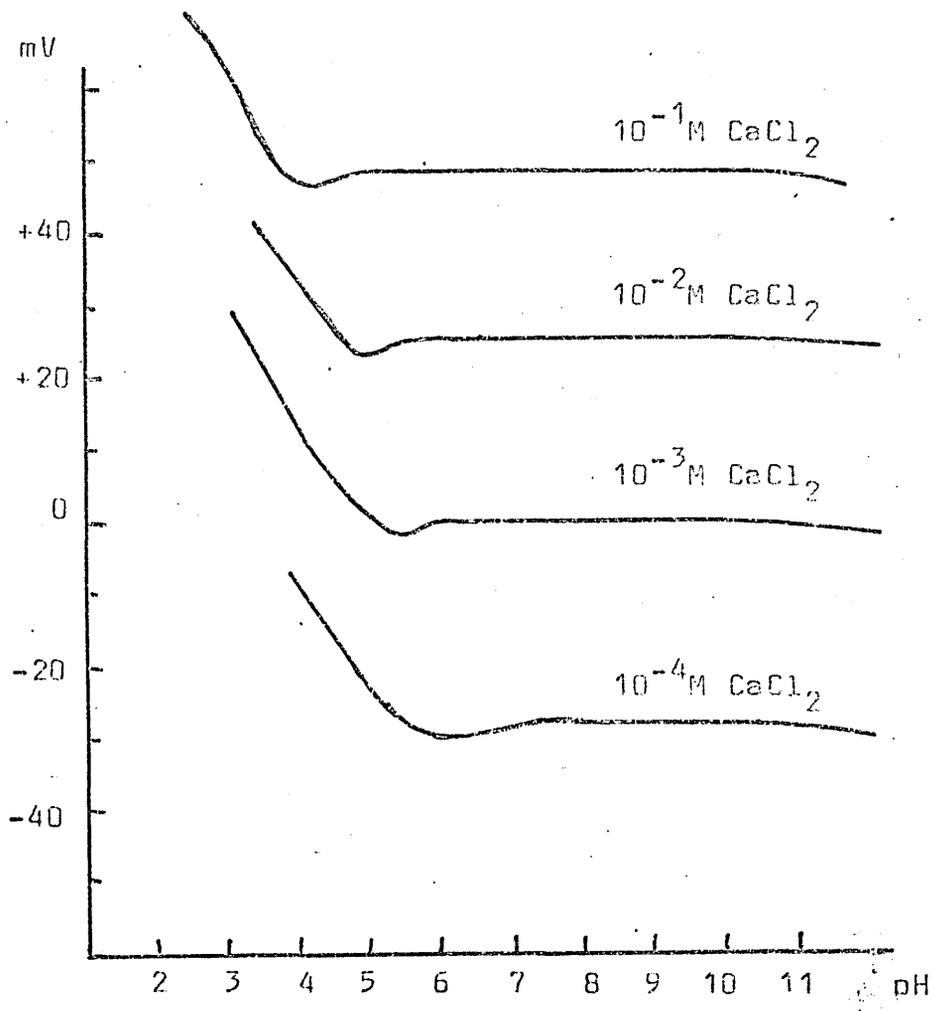


Figure 1-3 Potential -pH diagram for the Orion 92-20  
electrode at varying CaCl<sub>2</sub> concentrations.  
The characteristic 'dips' are clearly visible.

Membrane constituents:  
PVC 0.17g  
Ca(DDP)<sub>2</sub> .036g  
DOPP .36g  
THF 6cm.

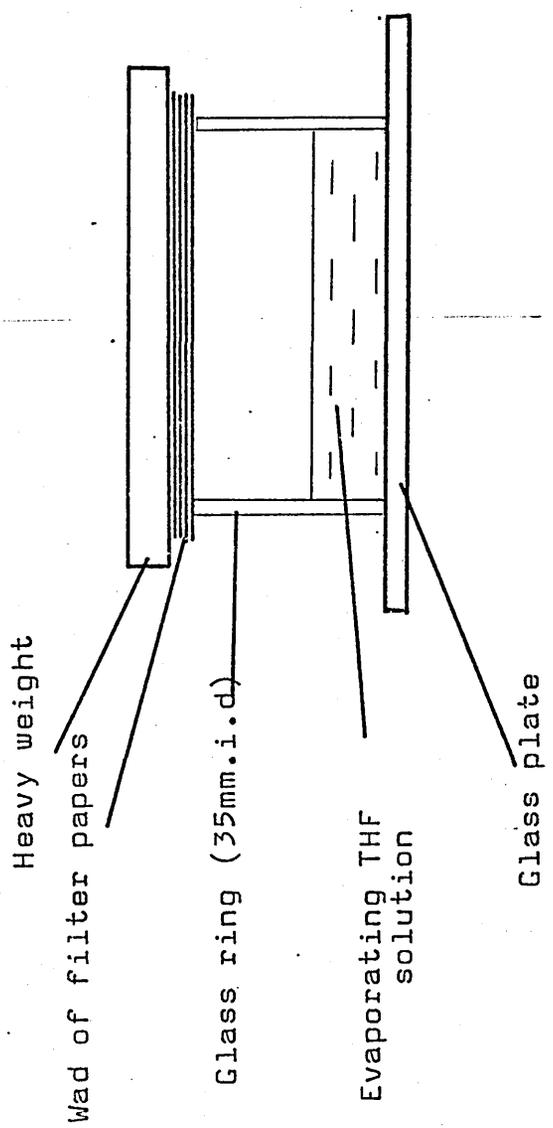


FIGURE 1-4. Production of a membrane for a calcium ISE.

To produce such an electrode<sup>73</sup>, PVC was mixed with an ion exchanger solution in tetrahydrofuran (THF); poured into a glass ring resting on a glass plate and the solvent allowed to evaporate slowly as depicted in Fig.1-4.

The resulting membrane was removed from the glass plate, cut into discs (6-10mm.dia.), stuck to the end of PVC tubing and with the insertion of a suitable internal reference half-cell (Ag.AgCl/0.1 M CaCl<sub>2</sub>) an inexpensive and simple calcium ion selective electrode was produced. It is this simplicity of fabrication which has meant that not only is the rather complex Orion 92-20 body now largely obsolete, but this approach has also simplified further improvements in the mechanical design of calcium ISE in addition to enabling great improvements in electrode performance to be brought about much more conveniently.

#### 1.2.8 Mechanical design advances.

With the advent of PVC matrix ion exchanger membrane it became possible to design electrode formats which either suited a particular application or which removed other drawbacks of the liquid membrane type of electrode (e.g. Orion 92-20). In particular, the exclusion of the microporous filter support not only has benefits in a simplified electrode design, but it removes the possibility of the filter exhibiting an electrochemical response such as has been noted for some filter/solvent systems<sup>67</sup>. Although not generally the case, it has been noted<sup>75,76</sup> that some solvent mediators alone show some calcium response, but it is believed that this response was due to trace acidic dialkylphosphate impurities in the particular batch of solvent-mediator used.<sup>76</sup>

In addition to the removal of the filter support, much effort has been devoted to the removal of the classical Ag.AgCl/Aq.Ca<sup>2+</sup> reference  $\frac{1}{2}$ -cell and this has been approached for a number of reasons and by a variety of methods.

#### 1.2.8.1 Coated wire ion selective electrodes<sup>77</sup>.

In this modification<sup>78</sup> the electroactive material may be mixed with PVC in a solvent and then dip-coated onto a metallic wire (Pt, Cu etc.)<sup>79</sup>. A layer of the ion exchange membrane is thereby formed on the wire giving a small, robust electrode with characteristics similar to a macroelectrode of conventional design using the same exchanger although the selectivity may, in some cases, be changed slightly. There is some concern, however, at the apparent lack of a thermodynamically definable internal reference element<sup>76,80</sup> which has led to a modification<sup>80</sup> of the membrane where a chloridized Ag wire is first coated with a hydrated reference medium membrane of 10% poly(vinyl alcohol) (PVA) in  $5 \times 10^{-3}$  M KCl and then immediately afterwards with a layer of ion exchanger/PVC. Alternatively, the end of the connecting wire may be coated with Ag.AgCl to give a stable internal reference element.<sup>134</sup> These techniques serve to introduce an internal reference element, but it has been suggested<sup>81,82</sup> that the coated wire configuration has a fortuitously inbuilt reference element due to the permeation of H<sub>2</sub>O and O<sub>2</sub> through the PVC enabling an oxygen, water/Pt half-cell to be set up at the PVC/Pt interface.



The resulting electrodes generally exhibit sub-Nernstian slopes, but their selectivity for Ca over Mg and Na is as good and often better than for the corresponding macroelectrodes. They have enabled calcium activity determination in single cells, such as muscle cells or ganglion cells from *Aplysa californica*.<sup>91</sup>

1.2.8.4 Chemically sensitive semiconductor devices (CSSD)<sup>92,93.</sup>

This very recent type of sensor brings together ion selective electrodes and semiconductor physics, but as yet, these devices have not found wide application due mainly to the technological problems accompanying their fabrication. Despite these very great problems, a calcium ion selective field effect transistor (ISFET) has been described<sup>94</sup> in which Ca bis-[di(1,1,3,3, TMBP)]/DOPP/PVC is cast directly onto the gates of a FET. Although exhibiting a near-Nernstian slope, problems of drift and short lifetime have limited the application of these sensors. Despite this, their minituarised form and low instrumentation requirement would give ISFETS many advantages if the technological problems can be overcome.

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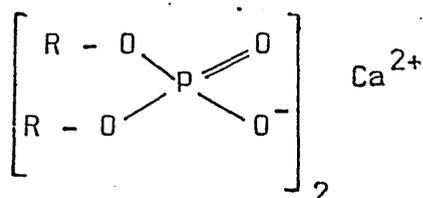
The mechanical design advances which have been made using PVC matrix ISE have been great. More important still though have been the advances in the chemistry of calcium ISE which the incorporation of alternative sensor/mediator systems into PVC matrices has enabled. The use of this approach has made it possible to investigate and optimise many of the parameters affecting electrode performance much more simply and inexpensively. The result of this is that PVC matrix membrane ISE now form a large group of ISE (not only for calcium) and the term 'liquid membrane ISE' has almost completely fallen into disuse in favour of terms such as 'plastic membrane' or 'PVC matrix' ion selective electrodes.

### 1.3 PVC Matrix Membrane Electrodes

The ever-increasing use of PVC as a matrix to immobilise a liquid ion exchange system is not surprising as this method allows great simplification and economy in the production of ISE. What is surprising, however, is that PVC remains almost the only polymer matrix in use after ten years despite difficulty of processing, requirement for internal stabilisers and intractable physical nature in absence of plasticisers. The reason for its importance as a matrix for calcium ISE may lie in its ready availability, but more importantly may be the fact that many good plasticising agents for PVC also impart extremely good selectivity upon organophosphate sensors. It is this last point which is crucial to the use of PVC matrix membranes for Ca ISE as the sensors commonly in use are calcium salts of organophosphoric acids such as  $\text{Ca}(\text{DDP})_2$  used by Ross<sup>48</sup>. Since the initial use of PVC<sup>50,72</sup>, much development work has been performed to improve the selectivity of calcium ISE and these improvements have largely revolved round modifications of the Ross exchanger on the one hand and the development of highly selective neutral carrier materials on the other. During various studies involving alteration of the sensor, the importance, but not necessarily the function, of the solvent mediator has been realised.

#### 1.3.1 Charged ion-exchanger systems.

This classification covers the negatively charged organophosphate systems analogous to that of Ross<sup>48</sup>. In general, the sensors are of the type:



where R may be an alkyl or aralkyl group.

They are Ca salts of organically disubstituted phosphoric acid and, as such, are capable of acting as ion exchangers when supported in a suitable diluent. The choice of this diluent is all-important to the selectivity of this ion exchange site. The diluent, or solvent-mediator as it has become known when used in ISE, is often another phosphoryl compound such as an alkylphenylphosphonate as used in the calcium ion selective electrode (Fig.1-1).

In the absence of a solvent mediator, a dialkylphosphoric acid will show a preference to form complexes with many polyvalent cations, particularly  $\text{Th}^{4+}$ ,  $\text{UO}_2^{2+}$  and  $\text{Fe}^{3+}$ , and, as such, can be of no use as calcium ISE. This fact may be of use to the nuclear industry in the manufacture of uranyl ion sensors<sup>95</sup>, but this application is seldom required. However, when a dialkylphosphate exchanger is placed in a strongly coordinating diluent, enhancement of the extraction of one ion in preference to many others may be seen. This synergistic extraction has long been known<sup>96,97,98</sup> and the case of  $\text{Ca}(\text{DDP})_2$  and DOPP acting synergistically to enhance the extraction of calcium ions over most other cations was the foundation stone for the development of calcium ISE.

The choice of a sensor/solvent-mediator system is not only based upon the synergistic extraction of the required ion, but also upon many other factors when used in an ISE. In particular, the sensor and mediator must be sufficiently hydrophobic to prevent their migration from the PVC matrix (or Millipore filter) into the test solution so losing the selectivity and increasing the

obtainable limit of detection of the ISE due to the loss of the calcium sensor salt. Consequently, the alkyl chain of the sensor should preferably be long in order to promote the required hydrophobicity, but the increase of the alkyl chain length above C<sub>12</sub> tends to result in 'gelling' within the membrane<sup>81,99</sup> giving rise to a deterioration of electrode performance. A didecyl chain length was chosen on the basis of the above factors and has resulted in good electrode performance<sup>72</sup>. Similar criteria also apply to the solvent mediator, but in this instance there are further complications in that the solvent-mediator is not merely a solvent for the sensor but it also influences many other factors;

- a) In a PVC matrix, the degree of plasticisation and, therefore, the mobility of species within the membrane is governed by the amount of solvent mediator.
- b) The ion-exchanger density is determined by the solvent:sensor ratio. Commonly, a 10:1 excess of solvent is used.
- c) The solvent mediator controls the final relative permittivity of the membrane phase.

With regard for the above points, the modification of both sensor and mediator and the subsequent analysis of the results not only permits the production of more selective ISE, but enables a greater understanding of the role of the solvent mediator in this type of membrane electrode.

#### 1.3.1.1 Sensor groups.

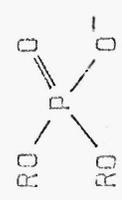
One of the drawbacks of the didecyl phosphate sensor was that electrodes using it tended to exhibit narrow pH ranges (5.5-10)

TABLE 1-3. The Development of Alkylphosphate Sensors for Calcium ISE.

Sensor	Mediator	Range $\Delta pCa$	Selectivity; $K_{CaM}^{pot}$										Membrane/format	Comments	R	
			Mg	Ba	Cu	Zn	Na	K	Mg	Ba	Cu	Zn				Na
DDP	DOPP	1-5	.015	.010	-	large	$10^{-4}$	$10^{-4}$	$10^{-4}$	$10^{-4}$	$10^{-4}$	$10^{-4}$	$10^{-4}$	millipore/liq. membrane	Ross electrode $Zn^{2+}, H^+$ interfere	
DDP	DOPP	1-5	.036	.010	.3	3	$10^{-5}$	$10^{-5}$	$10^{-5}$	$10^{-5}$	$10^{-5}$	$10^{-5}$	PVC matrix	Ross electrode, extended lifetime		
DEHP	DOPP	1-4.7	.057	.048	1.7	0.10	46	14					"	$M^+ = 10^{-2}M$ $M^{2+} = 10^{-3}M$		
HDOPP	DOPP	1-5	$2.5 \times 10^{-4}$	$10^{-4}$	$10^{-4}$	.06	$10^{-5}$	$10^{-5}$	$10^{-5}$	$10^{-5}$	$10^{-5}$	$10^{-5}$	PVC/Selectrode			
"	"	"	.062	.041	.038	.12	1.2	.01					PVC matrix	$M^+ = .05M$ $M^{2+} = 5 \times 10^{-4}M$		
HDTMBPP	DOPP	1-7	$10^{-3}$	-	-	-	$10^{-7}$	$10^{-7}$	$10^{-7}$	$10^{-7}$	$10^{-7}$	$10^{-7}$	PVC/ $\mu$ electrode	Biological studies		
"	"	1-5.5	.045	.041	.048	.56	.022	.018					PVC matrix	$M^+ = .05M$ $M^{2+} = 5 \times 10^{-4}M$		
"	"	"	.021	.009	.014	.3	.017	.018					"			

Sensors:

General formula

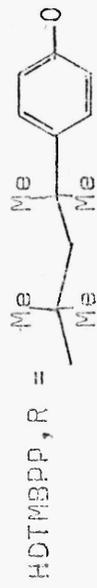


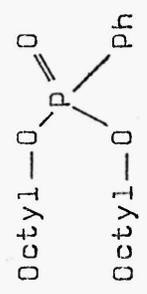
Mediator: DOPP

DDP, R =  $C_{10}H_{21}$  aliphatic.



HDOPP, R = 

HDTMBPP, R = 

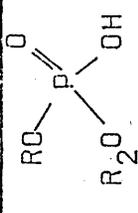
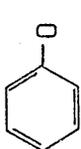
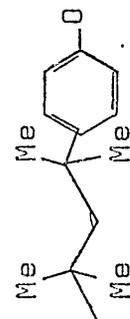
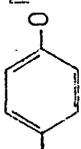


and showed 'dips' in the potential-pH diagram (e.g. Figure 1-3). For this and other reasons, modifications have been made to the original ion-exchanger (Table 1-3).

The 'dips' in the potential-pH plots have been found to coincide with maxima in the extraction efficiency of the sensors<sup>76,100,101</sup> and it has been suggested<sup>76</sup> that an increase in the electrophilicity of the alkyl chain would make the hydrogen atom more labile thereby increasing the pH range. Indeed, this was found to be the case both for di-4-octylphenylphosphate (HDOPP) and for di-4-(1,1,3,3-tetramethylbutyl)phenylphosphate (HDTMBPP). However, although the pH range was extended, the major benefit of these two systems was the great improvement in calcium selectivity, particularly over the transition metal cations (compare  $k_{CaCu}^{pot}$  values in Table 1-3). As can be seen, both these sensors give highly-selective calcium ISE, but it is preferable to use HDTMBPP as the starting material for its synthesis [4-(1,1,3,3-tetramethylbutyl)phenol] is more readily available than the linear analogue.

Cattrall and Drew<sup>81,100,102</sup> have examined the performance of several alkyl phosphate sensors for use in coated wire ISE and a summary of some of their findings may be seen in Table 1-4. These workers used di-(2-ethylhexyl)2-ethylhexylphosphonate solvent-mediator exclusively, rather than the DOPP used by other workers, but still found that the alkylphenyl substituents gave better selectivity than the alkyl systems and that the pH-independent region was extended to more acid values.

TABLE 1-4. The Effect of Different Sensors on the Selectivity of a PVC Matrix Coated Wire ISE with di (2-ethylhexyl)2-ethylhexylphosphonate as solvent-mediator.

SENSOR.	Range $\Delta pCa$	Selectivity Coefficient, $k$				
		Mg	Ba	Cu	Zn Na	
$R_1, R_2 = $  Di-(2-ethylhexyl)phosphoric acid HDEHP	1.5 - 3.4	.05	.009	4.95	69.6	.003
$R_1, R_2 = n - C_8H_{17}$ Di-(n-octyl)phosphoric acid, HDOP	2-3.7	.122	.007	.622	210	$10^{-3}$
$R_1, R_2 = C_8H_{17}$ Di-n-octylphenylphosphoric acid HDOPP 	1.6 - 4.2	.028	.008	.17	169	$10^{-3}$
$R_1, R_2 = $  Di-iso-octylphenylphosphoric acid IOPA (or HDTMBPP)	1.5 - 3.6	.005	.018	.62	47	$10^{-3}$
$R_1 = H, R_2 = C_8H_{17}$ Mono-octylphenylphosphoric acid H <sub>2</sub> MOPP 	1.5 - 3.2	.018	.002	.68	129	.011

Data from refs. 81, 100, 102

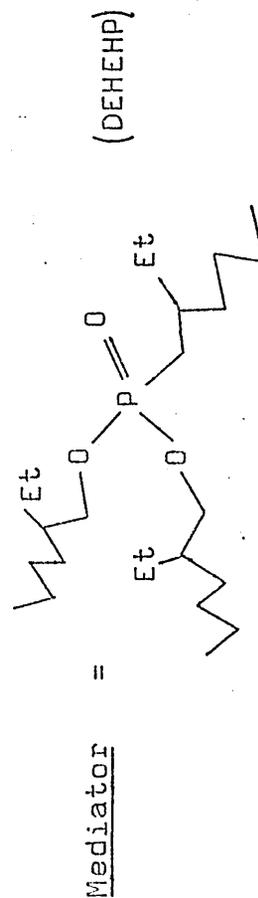


TABLE 1-5. The influence of a solvent mediator on the response of PVC membrane coated-wire ISE.

Sensor <sup>a</sup>	Mediator	Selectivity, K <sub>CaM</sub> <sup>pot</sup>									
		Mg	Ba	Sr	Na	K	Cu	Pb			
HDEHP	DEHEHP	.05	.009	.024	.003	.023	4.95	46.2			
	None	.197	.403	.399	.01	.05	2.11	2.69			
HDOP	DEHEHP	.006	.011	.012	.003	<10 <sup>-3</sup>	1.50	5.29			
	None	.082	.036	.055	.001	.006	.276	.510			
IOPA	DEHEHP	.005	.018	.011	<.001	0.11	.620	12	4		
	None	.14	.276	.512	.037	.138	2.31	.76	<		
H <sub>2</sub> MOPP	DEHEHP	.018	.002	.022	.011	10 <sup>-3</sup>	.680	11.9			
	None	.454	.582	.496	.087	.185	2.83	.2			

a.

For names/structures see Table 1-4. Data from reference 100.

Since these researches, attempts to use ring-substituted alkylphenyl phosphates have been made in efforts to further improve selectivity and remove the pH 'dips'. Bromination of the phenyl rings<sup>103</sup> resulted in poor electrodes due to the insolubility of the sensor in the mediator (DOPP). Other work involving nitration of the phenyl rings or the mediator<sup>104,105</sup> has resulted in the removal of the pH 'dips' using calcium bis(di-4-(1,1,3,3-tetramethylbutyl)-2-nitrophenylphosphate) sensor in conjunction with di-(n-octyl)-3-nitrophenylphosphonate solvent mediator. The use of this mediator with di-4-nitrophenylphosphate sensor<sup>104</sup> also exhibited no pH 'dip', but the sodium selectivity was poor ( $k_{CaNa}^{pot} = 0.6$ ) and the sensor was water soluble due to the lack of a hydrophobic alkyl chain. An investigation into the utility of calcium bis-4-(1,1,3,3-tetramethylbutyl)-2,6-dinitrophenoxide as a sensor for calcium ISE<sup>106</sup> resulted in an electrode showing poor selectivity. In general, an increase in electrophilicity by nitration does not appear to give any added selectivity, but does yield further information into the synergism between sensors and mediators. The sensor of choice at present, for calcium ISE appears to be HDTMBPP<sup>107</sup> as it offers synthetic availability with good electrode selectivity.

#### 1.3.1.2 Solvent-Mediators.

It has long been realised that the solvent mediator greatly influences the selectivity of the organophosphate sensors in calcium ISE. This is shown particularly strongly in Table 1-5 where the influence of the solvent mediator (DEHEHP) on the sensors studied by Cattrall and Drew<sup>81,100,102</sup> is easily seen.

TABLE 1-6. The effect of changing the solvent mediator on the selectivity of Ca ISE using Ca bis [4-(1,1,3,3-tetramethylbutyl)phenylphosphate] sensor in PVC.

Selectivity,  $K_{CaM}^{pot}$

Solvent mediator	Mg	Ba	Na	K	Mn	Cu	Zn	Interferent levels.
Diocetylphenylphosphonate	.045	.041	.022	.018	.12	.048	.56	a, b
Tributyl phosphate, (TBP)	.033	.036	.016	.013	.11	.027	.23	a, b
Triamyl phosphate	.031	.020	.01	.01	.069	.021	.22	a, b
Triocetyl phosphate	.18	.081	.097	.056	.56	.20	high	a, b
Tri 4-(1,1,3,3-tetramethylbutyl)phenyl phosphate	.045	.029	.026	.022	.091	.06	.51	a,b,
Dibutylsebecate	.03	.04	.5	.5	.05	.05	.03	b, c
Diethyl adipate	.04	.02	.3	.2	.08	.02	v.high	b, c

Date from Refs: 109  
110

- a.  $M^+ = 5 \times 10^{-2} M$
- b.  $M^{2+} = 5 \times 10^{-4} M$
- c.  $M^+ = 5 \times 10^{-3} M$

In the absence of solvent mediator there is a dramatic worsening of electrode selectivity for the weakly interfering cations (Mg,K,Na) but a marked improvement in selectivity over strong interferents such as the transition metal cations.

The most widely used solvent mediator is DOPP due to its ready availability, its remarkable enhancement of calcium selectivity and for its plasticising effect on PVC. Other solvent-mediators have been investigated<sup>108,109,110,111</sup> and results of some of these studies may be seen in Table.1-6 which indicate that the most selective calcium ISE over a whole range of other cations is that made from HDTMBPP with triamylphosphate solvent mediator. However, DOPP gives almost the same selectivity and remains widely used, although recent studies<sup>112</sup> suggest tri-n-pentylphosphate to be at least as good as DOPP when used with the newer octylphenylphosphate exchangers.

From the above data and other studies on the role of the solvent mediator<sup>113,114</sup>, in conjunction with the points raised in Section 1.3.1 it may be expected that the best mediators for calcium electrodes containing organophosphate sensors would be strongly-coordinating solvents, usually containing a phosphoryl group and capable of plasticising PVC when used in such a format. Additionally, it is noticeable that the relative permittivities of the mediators giving the best results for calcium ISE lie in the range,  $E = 5.0 - 8.3$ .

From the preceding section it is obvious that even subtle changes of solvent-mediator influence the selectivity of calcium ISE. It may be possible, therefore, to pick the sensor/mediator

TABLE 1-7    The effect on selectivity of varying mixtures of mediators.

Mediator composition		* Selectivity coefficient, $k_{CaM}^{pot}$	
Decan-1-ol	DOPP	Mg	Na
100% w/w	0% w/w	1.6	.070
83	17	0.79	.030
66	.33	0.1	.013
50	50	$8.6 \times 10^{-3}$	$6.1 \times 10^{-3}$
0	100**	$4.9 \times 10^{-4}$	$1.1 \times 10^{-3}$

\* Interferent level,  $[Mg^{2+}] = [Na^+] = 5 \times 10^{-2} M$ .

\*\* All membranes but this showed exudation of mediator.

Data from ref. 110

most suited to a particular analytical purpose<sup>100,102</sup> and in the extreme case, one may use widely differing mediators or mixtures of mediators<sup>108,110</sup> to invoke large changes of electrode selectivity. This approach has been employed<sup>108</sup> in the preparation of a calcium-magnesium (Water hardness) electrode, where use has been made of the fact that decan-1-ol as mediator with calcium bis (di-(2-ethylhexyl)phosphate) as sensor renders an electrode selective only for divalent cations over monovalent cations. If on the other hand, DOPP mediator was used, then a calcium selective electrode would result. The effect of using varying amounts of these two mediators is shown in Table 1-7 in the case of calcium bis-di(4-(n-octyl)phenyl)phosphate sensor.

Similarly, by selecting a suitable sensor and mediator, use may be made of the large zinc interference seen with many calcium ISE. In this way, a zinc-selective PVC matrix ISE has been reported<sup>115,116</sup> which, obviously, suffers from severe calcium interference.

### 1.3.2 Neutral Carrier ion exchangers.

In general, a neutral carrier molecule for use in the fabrication of ISE ought to satisfy several criteria<sup>117,118</sup>:

- a) the carrier must be composed of both polar and non-polar groups;
- b) the polar groups (typically containing oxygen as ligating atoms) should be capable of coordinating to a cation such that a 'cavity' is formed into which only the ion of interest will fit;

- c) the non-polar groups should be arranged in such a way that they form a hydrophobic shell around the ion-cavity enabling the carrier-cation complex to be solubilised in an organic medium;
- d) the carrier must be sufficiently rigid to allow the formation of a stable 'cavity' around the cation of interest, but should retain some flexibility to enable sufficiently rapid cation-exchange.

Several types of neutral carrier molecules meeting many of the above criteria have been used in the fabrication of calcium ISE.

#### 1.3.2.1 Dioxaalkane diamides.

Many such compounds have been synthesised and tested for calcium selectivity by Simon's group.<sup>117,119</sup> The carrier generally used for calcium ISE<sup>120</sup> is N,N'-di((11-ethoxycarbonyl)undecyl)-N,N'-4,5-tetramethyl-3,6-dioxaoctane diamide whose structure is shown in Figure 1-5.

Early use of this material in calcium ISE showed large calibration deviations in the presence of e.g.  $\text{ClO}_4^-$  due to anion permeation into the membrane, but the incorporation of lipophyllic anions was shown to reduce the effect<sup>121,122,123</sup>. The selectivity of this sensor, when incorporated with a suitable solvent, into a PVC matrix ISE is extremely good (e.g.  $K_{\text{CaMg}}^{\text{pot}} = 3 \times 10^{-5}$ ,  $K_{\text{CaNa}}^{\text{pot}} = 5.7 \times 10^{-3}$ ) and the choice of solvent is perhaps not as critical as with charged alkylphosphate sensors. However, it is generally the case that  $K_{\text{CaM}^+}^{\text{pot}}$  values decrease with increasing relative permittivity of the solvent, 4-nitroethylbenzene ( $\epsilon=24$ ) being particularly favoured<sup>124</sup>.

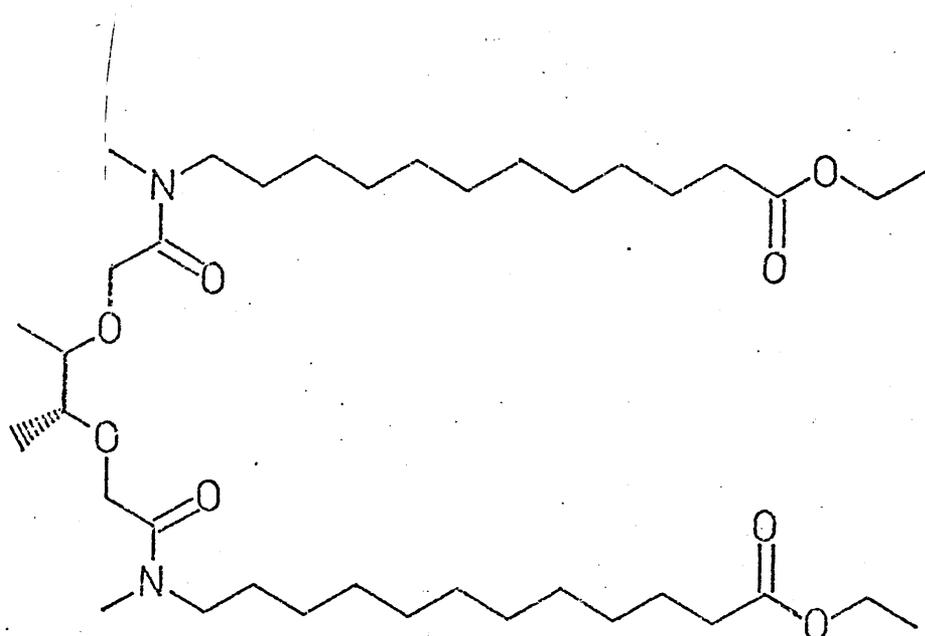


Figure 1-5. Structure of N,N'-di[[11-ethoxycarbonyl]undecyl]-N,N'-4,5-tetramethyl-3,6-dioxaoctane diamide.

The selectivity of such systems is very impressive, but they show a lack of general acceptance when compared to the organophosphate systems. This may be due to the much more difficult synthesis, or to other underlying factors such as the poor pH performance recently reported<sup>111</sup>.

#### 1.3.2.2 Poly (alkylene glycol)-calcium complexes.

Tetraphenylborate salts of calcium poly(propylene glycol) complexes have been used as sensors for calcium ISE in conjunction with either phosphonate or phosphate mediators<sup>125,126,127</sup>. When used with DOPP, the selectivity over magnesium was good ( $k^{\text{pot}} = 0.06$ ), but the electrodes suffered from severe Li and Na interference ( $k^{\text{pot}} = 2230, 1.5$  respectively and generally gave short lifetimes.

#### 1.3.2.3 Antibiotic A23187.

This carboxylic acid antibiotic has been used in a calcium selective electrode<sup>89,128</sup> in which the sensor was incorporated in a cellulose membrane in nitrobenzene. However, the performance of this electrode was very poor generally. Its selectivity order was  $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ , besides showing poor  $\text{Na}^+$  selectivity, and this sensor has been abandoned in favour of more selective and easily available materials.

#### 1.3.2.4 Cyclosiloxanes.

Recent studies<sup>129</sup> using tetracosamethyl cyclododecasiloxane in PVC on a coated Pt plate electrode indicate another type of complex which might be used in a calcium ISE. The membrane contained only the sensor complex and PVC and showed a Nernstian response  $5 \times 10^{-5}$  to  $10^{-2} \text{M}$ , but selectivity was generally poor. The electrode exhibited a pH range from 1.5 - 5 and its selectivity for calcium

over  $\text{Na}^+$  and  $\text{K}^+$  was limited ( $k^{\text{pot}} = 1265,115$  respectively at  $10^{-3}\text{M}$  interferent concentration) although selectivity over zinc ion was good. Dynamic response times were less than 10s and the system has since been patented.<sup>130</sup>

The preceding sections indicate the wide range of materials investigated for use in calcium ISE and show that, at present, the preference is for the di-iso-octylphenylphosphate sensor (HDTMBPP) in conjunction with DOPP. Notwithstanding this, ISE based on a diamide neutral carrier may be gaining some acceptance, particularly in the all-important clinical area<sup>131</sup>. Contrary to the development and diversification which has taken place with sensors and mediators, there have been few studies aimed at replacing PVC as the matrix material or at modifying the PVC matrix.

#### 1.4 Alternative membrane materials to PVC.

The successful use of PVC as a matrix for calcium ISE has continued over the last decade. Although the use of PVC has considerably simplified the fabrication of calcium ISE, PVC is not an ideal matrix material in many respects.

Firstly, PVC is a glassy polymer and, in order to render this material suitable for use as an ion-exchange membrane in an ISE, the material must be plasticised. In the case of calcium ISE, it is fortunate that good plasticisers for PVC also tend to be good solvent mediators, although the high levels of plasticiser generally used (60-70%), result in membranes which are usually flaccid and may require additional support. Also, PVC requires stabilisers to maintain its physical properties and these are usually organometallic

compounds which may exhibit some electrochemical response. The removal of these stabilisers results in a marked decrease in the stability of PVC to heat and U.V. light and so the use of other materials may be advantageous.

An early calcium ISE<sup>58</sup> used collodion as a matrix to some effect, although the later work of Griffiths<sup>99,132</sup> who used collodion, some celluloses and pyroxylin matrices for calcium ISE, showed these materials to give poor electrode performance. This was attributed to their lack of hydrophobicity which allowed much faster leaching out of the sensor/mediator resulting in truncated lifetimes and poor stability.

A study<sup>133</sup> using synthetic polymers other than PVC for neutral carrier type ISE found that poly(methylmethacrylate), poly(styrene) and a polyamide gave electrodes with very poor physical and electrochemical properties when compared to PVC. Schäfer<sup>135,136</sup> employed poly(vinylisobutylether) with the intention of investigating selectivity differences produced by the use of a different matrix for a calcium ISE. However, he used the components for a divalent ion electrode and, as for the PVC counterpart, found selectivity for divalent cations rather than calcium alone but also showed the incompatibility of decan-1-ol with poly(vinylisobutylether).

No further studies have investigated the mere replacement of PVC as a matrix material and the foregoing research merely reinforces the position of PVC as a matrix material for calcium ISE. However, despite the obvious advantages of PVC, such a system suffers from a drawback in that the polymer is merely acting as a

'trap' in which the ion-exchange solution is entangled. The result of this is that the ion-exchanger is able to migrate from the membrane and so the useful lifetime is limited. This lifetime may be calculated on the basis of several assumptions<sup>137</sup> with periods of months usually required for the migratory loss of the sensor/mediator. In adverse chemical or thermal conditions, or in flowing streams, however, the leaching of exchanger may proceed at a much faster rate leading to lifetimes more in the order of days. It is perhaps for this reason that our attention has turned to the covalent binding of the sensor group with the intention of giving a non-leachable sensor with the subsequent increase in lifetime.

Other workers have, to this end, phosphorylated a poly (vinyl chloride)-poly(vinyl acetate) copolymer with decyl dihydrogen phosphate<sup>138</sup> to produce a polymer with 'grafted' alkyl-phosphate sensor sites. In order to produce a membrane for a calcium ISE using this material, the calcium form of the phosphorylated polymer was mixed with PVC and DOPP and the resulting electrode exhibited electrochemical properties in many ways similar to one using PVC with the Orion exchanger<sup>72</sup>. Although the sensor groups were covalently bound, and therefore, non-leachable, the solvent mediator was merely entangled and the expected increase in lifetime was not observed.

Additionally, a surfactant ISE has been produced<sup>139</sup> using functionalised PVC in which the sensor groups were covalently bound. In this case, also, the mediator (tricresylphosphate) was not

bound in and so the lifetime was again limited by the loss of this material.

The utility and possibility of covalently binding sensors to polymers have been demonstrated and the use of a polymer or another covalently-bound mediating function might be expected to improve calcium ISE still further. It is this approach which has been used in the work to be described in this thesis.

#### 1.5 Aims of this work.

The general aims of the work described here were to develop a novel type of ion-selective electrode for calcium and to evaluate its applicability to potentiometry, monitoring and process control; and to contribute to the knowledge of the mechanisms which control electrode selectivity. To try and achieve these aims a fundamentally new approach has been adopted to the design and construction of ion-selective polymeric-membrane electrodes through the immobilizing, by covalent bonding to polymeric matrices, of suitable ion exchange groups.

In particular the possibility of covalently binding phosphate groups into a polymeric material to give a calcium ion-selective electrode has been investigated.

CHAPTER 2

PRODUCTION OF MEMBRANES WITH  
COVALENTLY BOUND SENSOR GROUPS

## 2.1 Introduction.

The possible advantages to be gained from covalently-binding a dialkyl ion exchange group to a polymer for use in a calcium ISE have been indicated in the previous chapter. In particular, it might be expected that a longer electrode lifetime would result using this approach. In addition, the limit of detection (LOD) of such an ISE might be found to be lower than that of a PVC matrix membrane electrode. The LOD of the latter type having been shown<sup>140</sup> to be limited to  $4 \times 10^{-5} M$  by the dissolution and subsequent dissociation of the sensor (a calcium salt) from the membrane into the test solution. Such dissolution would not occur if the sensor were covalently bound.

There are many possible approaches to the incorporation of a functional group (e.g. a phosphate) into a polymer.<sup>141</sup> In principle, the active groups may be:

- 1) part of the main chain;
  - 2) linked to a polymer chain as a pendant group;
- or,
- 3) at the end(s) of a low or moderate molecular weight polymer.

The first approach results in the formation of a polymer with the general form:



The phosphate resins produced by Kennedy<sup>142,143</sup> were of this type except that a linear chain was not being formed as

the matrix was highly cross-linked. This high level of cross linking was due to the multifunctional monomer used. The monomer used was triallylphosphate which was polymerised using free-radical initiation. The resulting glassy polymer was highly insoluble and when crushed and hydrolysed a functionalised polymeric ion exchange bead was produced. The active exchanger of the polymer bead was a dialkylphosphate which was used to exchange ions of interest to the nuclear program.<sup>144,145</sup> Despite a high exchange capacity, poly(triallylphosphate) cannot be used in membrane form due to its glassy nature brought about by the high degree of cross-linking and short runs.

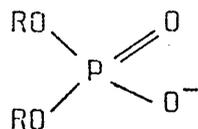
In the second approach functional groups are attached to a polymer whose properties are already well characterised. In this way, organophosphorus moieties have been grafted onto polymeric fabrics resulting in fabrics showing fire-retardant properties.<sup>146</sup> Polymers and copolymers containing styrene main chains have been grafted with phosphates<sup>147,148</sup> or phosphonates<sup>149</sup> whilst phosphate groups have been introduced into a styrene copolymer to yield a cationic ion exchange resin.<sup>150</sup> A recent report<sup>151</sup> has described the covalent bonding of a neutral carrier ion-exchange moiety to a styrene-divinylbenzene copolymer.

The third approach to a functionalised high molecular weight (M.W.) polymer requires fine control of the polymerisation

reaction. It has been used successfully to produce PVC with either quaternary alkylammonium or sulphonic acid end groups which were used in the production of surfactant selective electrodes.<sup>139</sup>

Of the three approaches possible, the second, in which a well-characterised polymer is used, is the most versatile and was the approach adopted for this study.

The ion exchange group normally used for the calcium selective electrode is the dialkylphosphate unit;



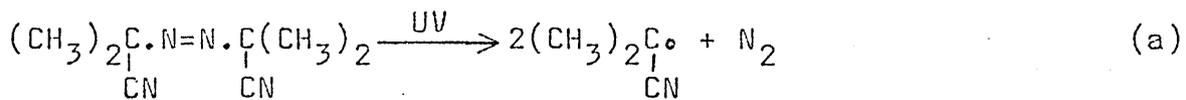
From the work of Kennedy<sup>142,143</sup> it was known that triallylphosphate (TAP) polymerised easily - forming short chains and resulting in a highly cross-linked network. In order to generate a calcium selective ion exchange group it would be necessary to hydrolyse any membrane containing TAP.

The polymer required was one which was readily available, easily processible and was well-characterised. In addition, it should show good physical strength, be hydrophobic and contain reactive groups to enable the monomer to be covalently bound to it. It should, however, not be so reactive that manufacture or subsequent use would cause excessive degradation. The polymer selected was a triblock elastomer, styrene-b-butadiene-b-styrene (SBS) which met all of the above requirements to some extent. The proposed reaction for incorporating the

dialkylphosphate sensor into polymeric SBS was free-radical initiated solution polymerisation of SBS with TAP monomer, followed by alkaline hydrolysis.

## 2.2 Synthetic approach.

The polymerisation reaction employed was a free-radical initiated addition polymerisation. The reaction involved three distinct steps; initiation, propagation and termination, shown in Figure 2-1. In step (a), the initiator 2,2'-Azobis (2-methylpropionitrile)ABIN, disproportionates under the influence of ultra violet (U.V.) radiation to form free-radicals,  $R\cdot$ . These free radicals are able to propagate the reaction by attacking the C=C double-bond in the butadiene chains. In the instance shown, (b), reaction is with the 1,2-butadiene pendant unsaturation forming a polymeric free-radical at (c). This radical may then react with the trifunctional monomer (TAP) to yield a phosphoryl group covalently-bound to the polymer, (d). In fact, many alternative propagation steps are possible, but most of these will result in bonding of the monomer to the polymer. In the instance shown, the free-radical (d) may further react e.g. with another section of the butadiene chain (e) resulting in chain cross-linking. Termination may occur by radical combination or by hydrogen abstraction. The terminating radicals may be from other sections of the polymer, monomer or initiator. The final polymer will have a cross-linked three-dimensional structure as TAP is a trifunctional monomer which will not give long linear poly (TAP) runs but will promote cross-linking.



ABIN

R•

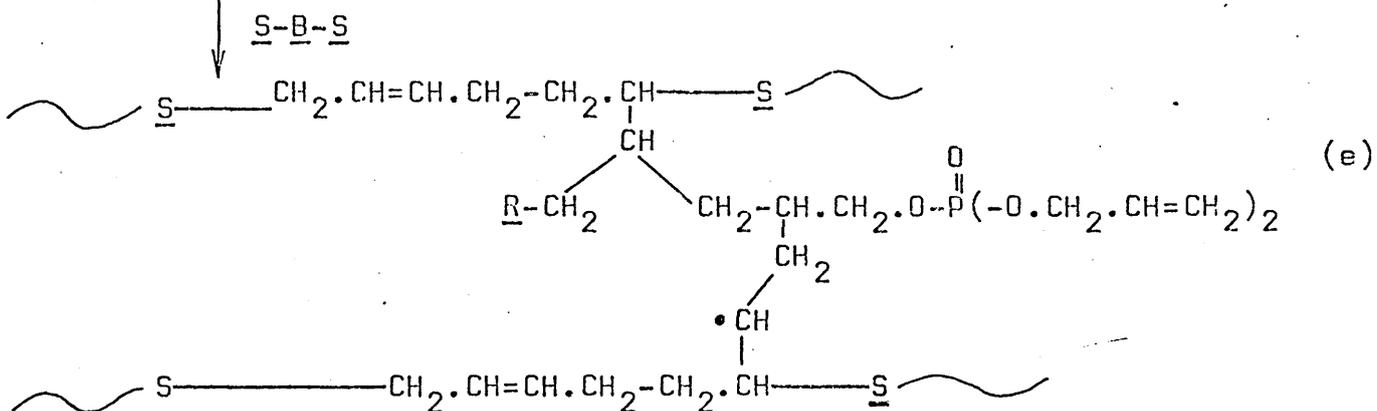
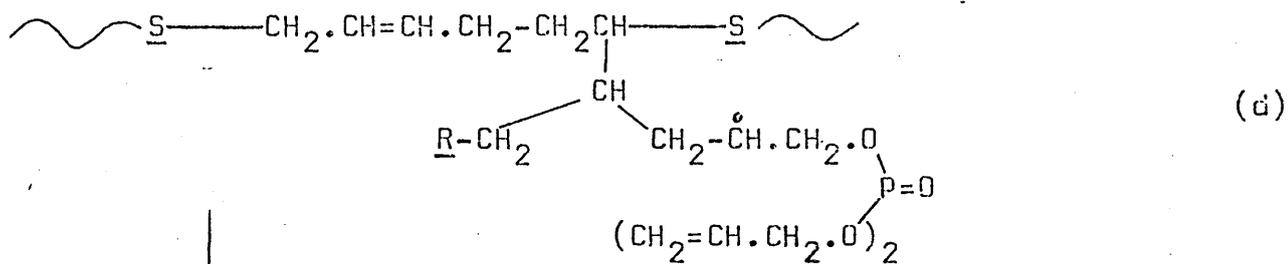
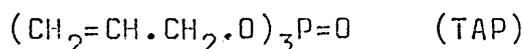
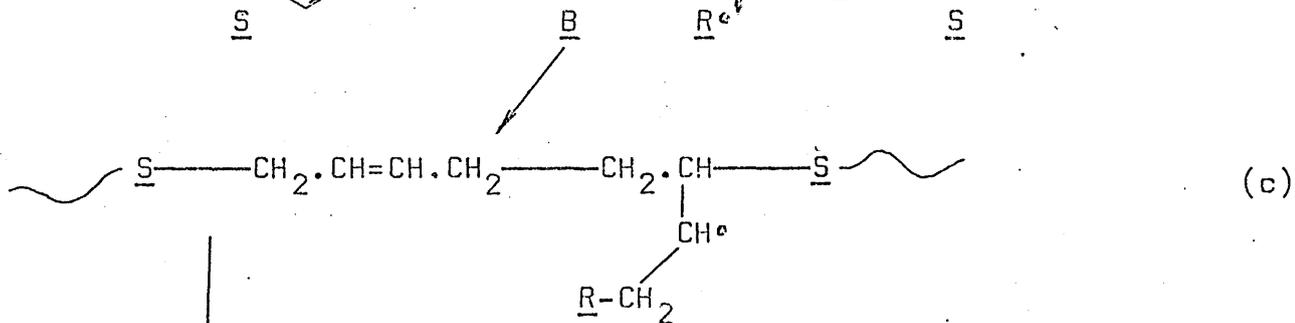
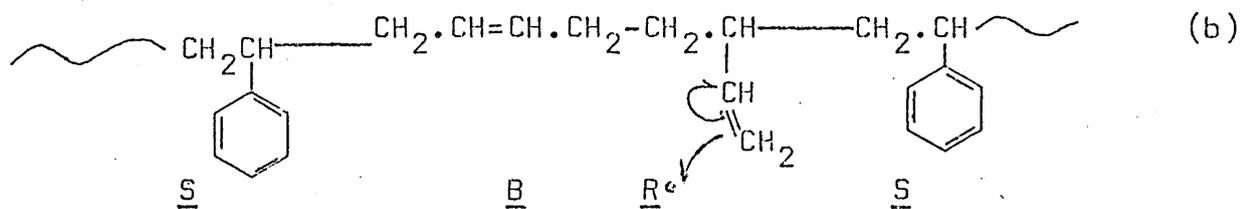


Figure 2-1      Immobilisation of phosphate groups.

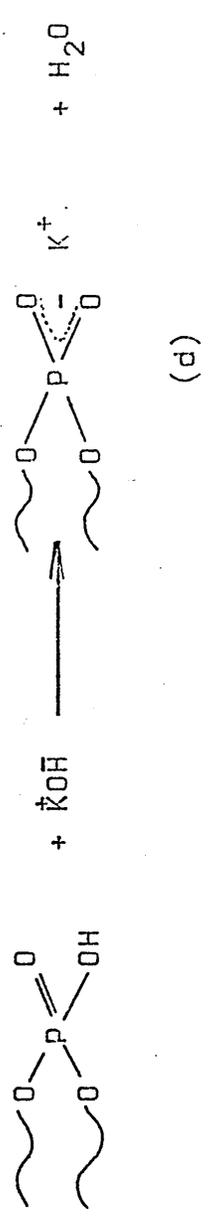
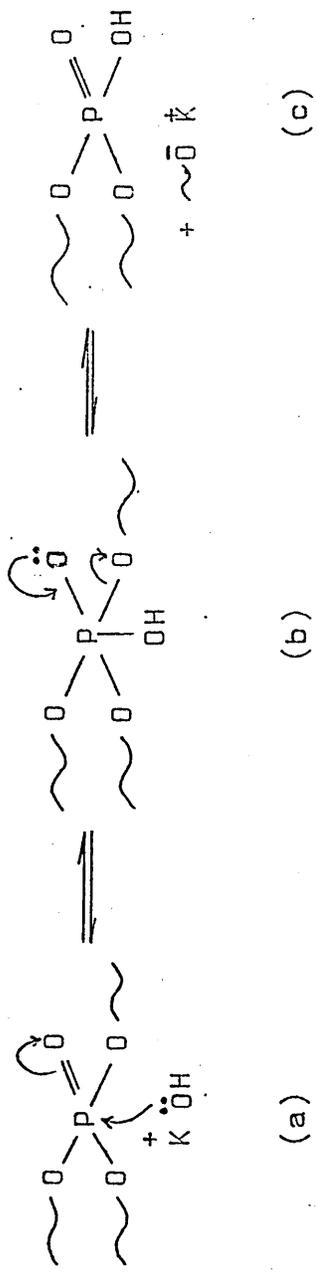


Figure 2-2. Hydrolysis of the pendant trialkylphosphate grouping.

Having produced the membrane containing covalently-bound phosphoryl groups it was necessary to hydrolyse in order to produce the active dialkylphosphate exchanger. This process may be seen in Figure 2-2 where the trialkyl phosphate (a), in which all the alkyl groups may or may not be attached to the polymer, was subjected to alkaline hydrolysis. Nucleophilic attack at phosphorus occurred forming an intermediate (b), which, through elimination of one alkoxy group, formed a dialkyl phosphoric acid (c). In the presence of base this will exist as the resonance-stabilised dialkylphosphate anion (d).

Further hydrolysis to the mono-alkylphosphate is very unlikely under mild alkaline conditions due to the high stability of the anion (d). Even though the phosphate may have only been anchored by one link in (a), this anchor is likely to remain in favour of loss of one of the alkyl groups. Thus, a polymeric membrane containing a covalently-bound and largely cross-linked

$\text{P} \begin{array}{l} \text{=} \text{O} \\ \text{---} \text{O}^- \end{array}$  group may be generated.

## 2.3 Experimental.

### 2.3.1 Reagents.

#### 2.3.1.1 Poly(Styrene-b-butadiene-b-styrene) triblock elastomer (SBS).

The material used throughout this study was SBS 1101 (Cariflex Styrene Butadiene Rubber, Shell Chemicals, London). Gel permeation chromatography indicated a weight average molar mass,  $\bar{M}_w = 14.5 \times 10^4 \text{ g.mole}^{-1}$  and a number average molar mass,  $\bar{M}_n = 9.74 \times 10^4 \text{ g.mole}^{-1}$ . The amount of triblock SBS polymer was

70% m/m, that of diblock SB, 26% m/m and the amount of homopolystyrene S, was determined to be 4% m/m. The total polystyrene content was determined by 100 MHz proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H-nmr) to be 27% m/m. 300 MHz. <sup>1</sup>H-nmr indicated 90% 1,4-butadiene and 10% in the 1,2-configuration.

In order to remove stabilisers, which would retard the proposed free-radical reaction, the polymer was purified. This purification involved dissolution of the polymer in THF (>24 hrs. at room temperature) and precipitation into rapidly-stirred methanol cooled in ice. The resulting white fibrous material was filtered, dried under vacuum at temperatures <35°C and stored in the dark.

#### 2.3.1.2 Tetrahydrofuran (THF).

Tetrahydrofuran (BDH, Poole, Dorset) was dried over sodium wire for 24 hours and then refluxed over calcium hydride and potassium metal and under nitrogen for a further 12 hours before use to ensure removal of traces of moisture. Clean, dry THF, free from stabilisers was produced by this technique and was freshly distilled under N<sub>2</sub> for use. It was found essential to minimise air and moisture contact, best results being given from THF used quickly after minimal exposure to air and light.

Hazards: The THF produced is fully destabilised and should not be left in contact with air and in direct sunlight due to the possibility of formatic unstable peroxide. The distillation of THF

from lithium aluminium hydride should be avoided in preference to the use of  $\text{CaH}_2$ .

#### 2.3.1.3 Triallyl Phosphate (TAP).

This material was obtained commercially (Aldrich Chemical Co., Gillingham, Dorset) and distilled under reduced pressure to give a clear colourless liquid which was stored at  $4^\circ\text{C}$  in the dark.

Hazard: Triallyl phosphate is a cancer suspect agent.

#### 2.3.1.4. 2,2'-Azobis(2-methylpropionitrile), (ABIN).

The white, powdery crystals were obtained commercially (BDH, Poole, Dorset) and recrystallised twice from hot methanol. The resulting needles were stored at  $4^\circ\text{C}$  in the dark and were found to be stable for long periods.

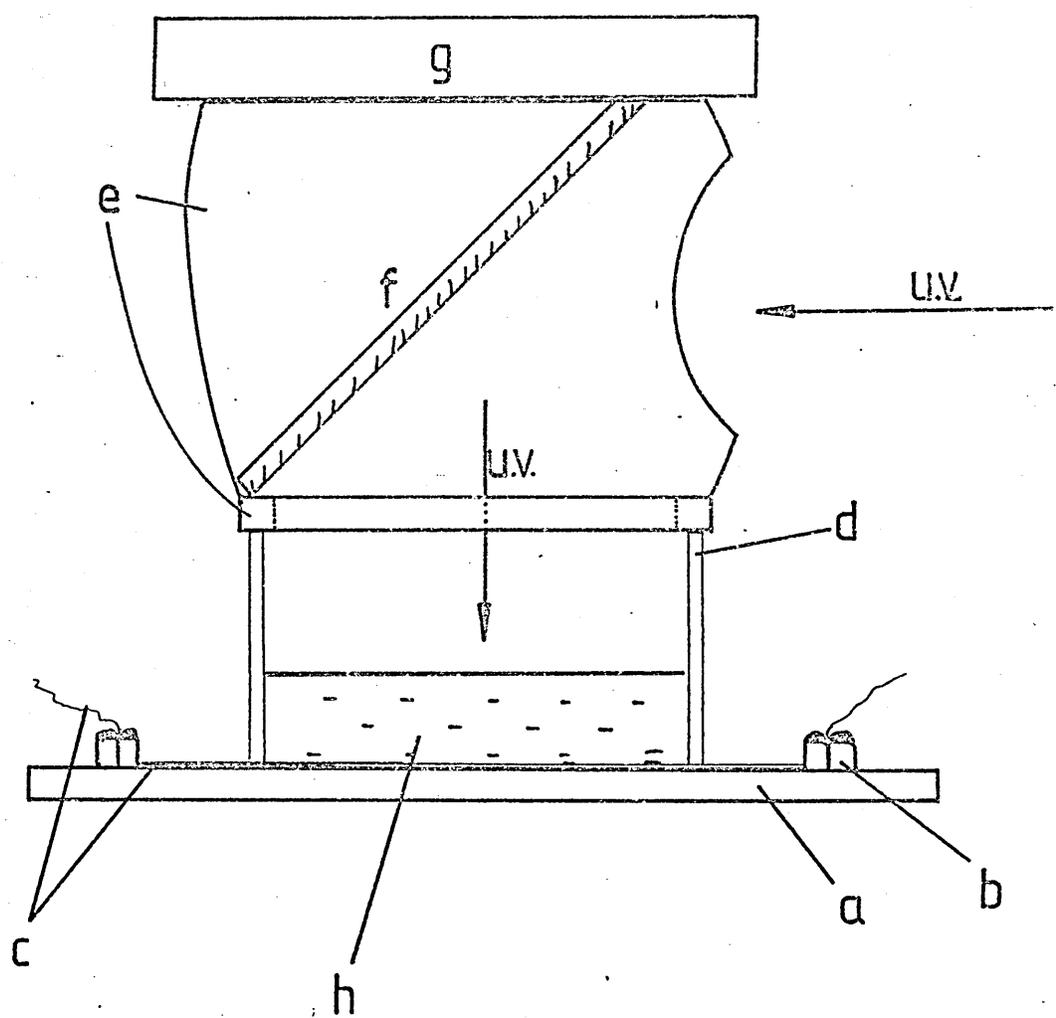
Of the other initiators used, benzoyl peroxide (BDH) was recrystallised from methanol and any others were used as received unless a stabiliser was present.

#### 2.3.2 Solvent casting.

4g of the purified polymer (SBS) were dispersed in  $50\text{cm}^3$  freshly distilled THF and allowed to dissolve over a minimum period of 24 hours. The required quantities of monomer and initiator were then dissolved in the minimum quantity of THF and mixed with the polymer solution. The resulting mixture was then allowed to stand for at least 30 minutes before being poured into the 95 mm i.d. glass ring (d) in the assembly shown in Figure 2-3. A pure cellophane film (c) (W.E. Cannings Ltd., Bristol) was stretched using a wooden embroidery ring (b) and

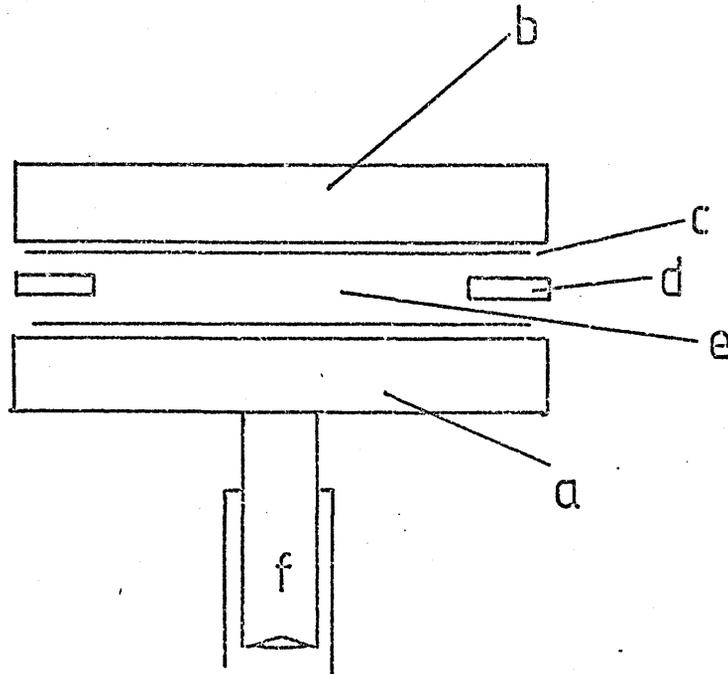
Figure 2-3

Casting apparatus



- a. Glass plate
- b. Embroidery ring
- c. Cellophane film
- d. Glass ring (95mm i.d.)
- e. Weight/mirror support
- f. Front-silvered mirror
- g. Weight
- h. Casting polymer solution.

Figure 2-4      Hydraulically operated hot press.



Key to figure:

- a. Lower heated plate
- b. Upper heated plate
- c. Melinex sheet
- d. Stainless steel mould former
- e. Mould space
- f. Hydraulic ram

acted as a gasket between the glass ring and the plane glass plate (a). The front-silvered mirror (f) was arranged such that incident radiation was directed normally onto the curing polymer solution. The combined weight and mirror support (e) was the valve guard from a gas cylinder and additional weight (g) could be added as required. The 250W ultra violet source was an Osram ME/D medium pressure mercury discharge lamp (Osram/GEC, London) which was situated 0.75m from the centre of the glass ring.

### 2.3.3 Hot pressing.

The press used (see Figure 2-4) had two 30cm-square plates (a,b) which were capable of being electrically heated to 350<sup>o</sup>C and hydraulically raised to 30 tons force on the ram, (f). In order to produce a membrane of the required thickness, a stainless steel former (d), 10cm square and 0.5mm thick was used and this was flanked on either side by sheets of Melinex polyester film (ICI Plastics, Welwyn Garden City, Herts). The purpose of this film (c) was to give smooth surfaces to the membrane and, when coated with a mould release agent (D55 Mould Release, Ind.Science Ltd., Dover, Kent) it allowed removal of the polymer membrane. Several techniques for the mixing of reagents prior to processing in the press were investigated.

#### 2.3.3.1 Mechanical blending.

Two very simple examples of this technique were used. In the first, the polymer (8g SBS) was shaken in a flask with the monomer (TAP - a liquid) and the initiator (ABIN - a solid) for 15 minutes and then introduced into the mould. In the second,

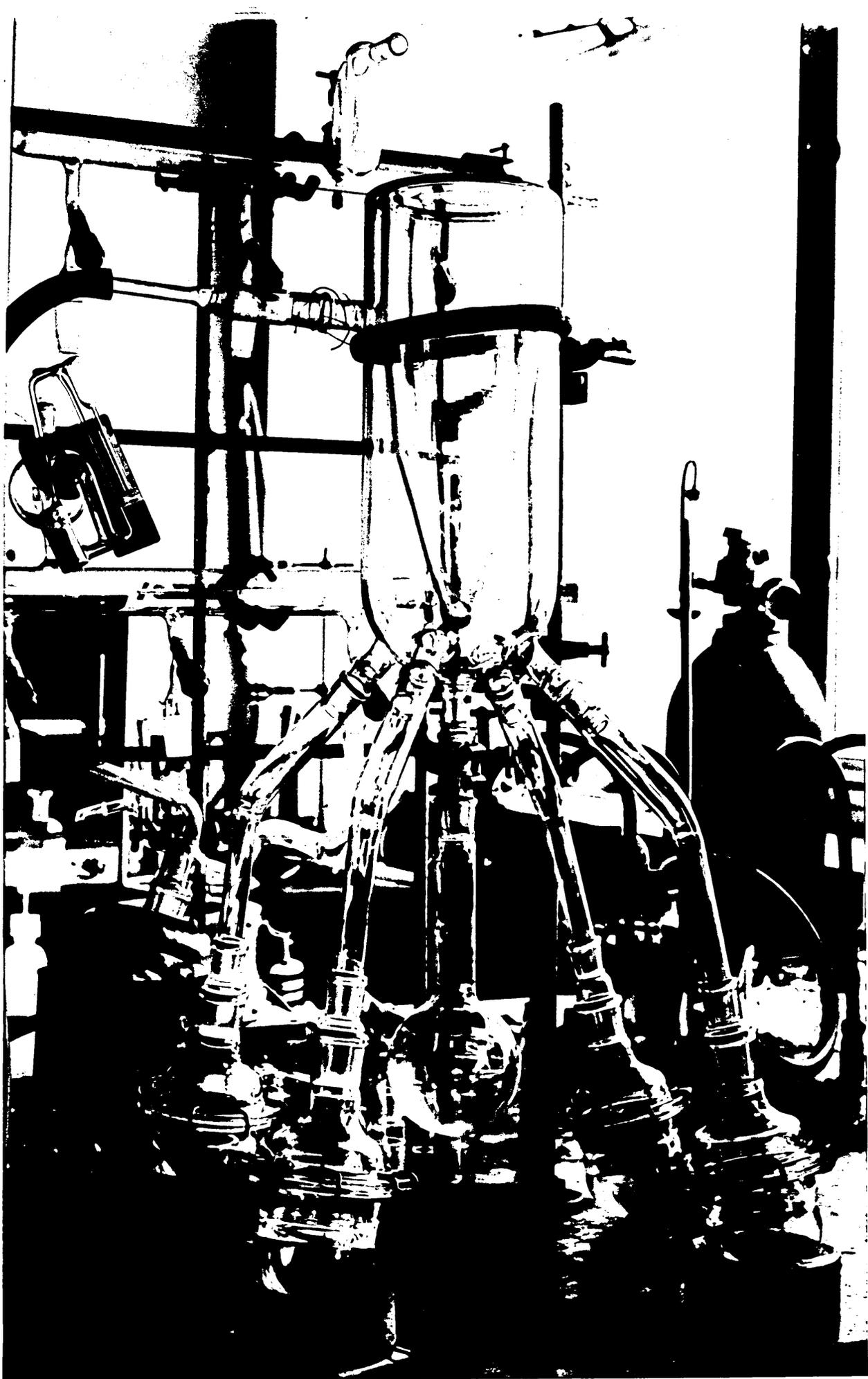


Plate 2-1 Lyophilization apparatus

the polymer was spread in the mould and the other reactants poured on top allowing the mutual dispersion of molten reactants to occur thermally in the press.

#### 2.3.3.2 Solvent coating.

A solvent was chosen which was a solvent for the monomer and initiator, but which was a non-solvent for the polymer. Thus, 8g of finely-divided, reprecipitated SBS were placed in a flask containing the other reactants in 150cm<sup>3</sup> methanol. The solvent was then removed slowly under vacuum on a rotary evaporator resulting in SBS coated with the other reactants which could then be pressed.

#### 2.3.3.3 Lyophilysis.

This process produced a wholly-homogeneous elastic prepolymer mixture by the use of freeze drying. The reactants were dissolved together in THF over a 24 hour period allowing them to become completely intermixed. The solvent was then removed under vacuum at ~5<sup>0</sup>C and trapped on a liquid nitrogen-cooled cold finger. The apparatus used (Plate 2-1) enabled 4 samples to be freeze-dried simultaneously. The clear, elastic prepolymer which was formed after careful evaporation over a 4-6 hour period could be removed from the resin kettles and placed directly into the press mould. N.B. The use of vacuum grease in the apparatus must be strictly avoided.

#### 2.3.3.4 Solvent casting followed by hot pressing.

In this method, a membrane was first formed using the solvent casting technique described in Section 2.3.2 without the use of U.V. irradiation. The resulting membrane could be

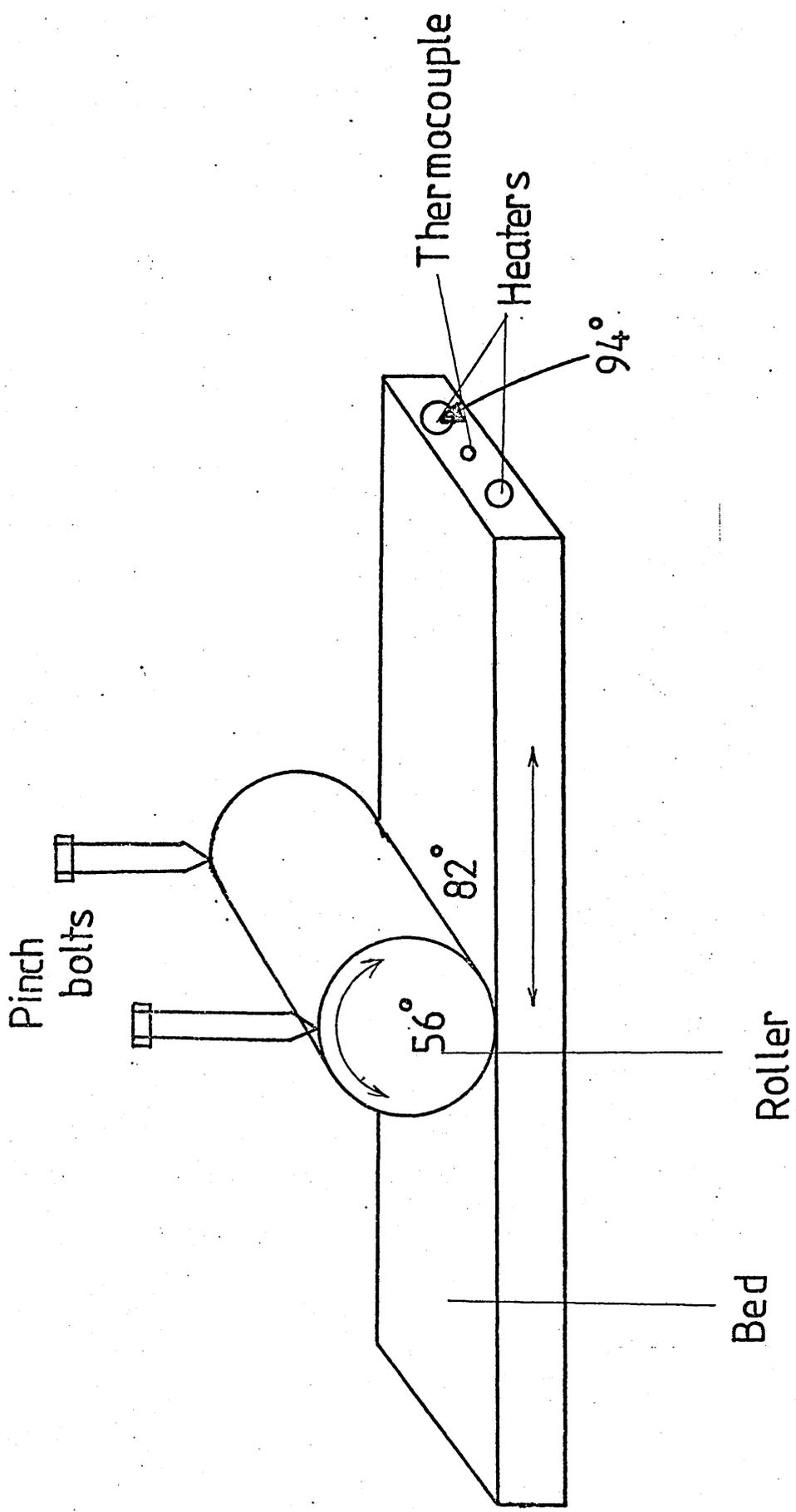


Figure 2-5      RAPRA Micro-Mill      (Schematic)

simply transferred from the casting apparatus to the press.

#### 2.3.3.5 Hot milling.

A RAPRA Micro-Mill (RAPRA, Shawbury, Shrewsbury, Salop) was used, the essential features of which are shown schematically in Figure 2-5. In practice, the polymer was placed on the heated bed and the pinch between the roller and the bed adjusted by means of the two pinch bolts. The roller was rotated one revolution first one way and then the other and as this was happening, the bed moved longitudinally as indicated. The combined effects of rolling, heating and pinch produced a polymer paste into which the other reactants were repeatedly folded to yield a homogeneous prepolymer.

#### 2.3.4 Determination of Phosphorus.

The method used to determine P was to acid digest the samples followed by a molybdenum blue spectrophotometric technique. A 5mm diameter section of membrane was placed in a boiling tube (alternatively, a micro-Kjehldahl flask may be used) and 4cm<sup>3</sup> concentrated sulphuric acid (Analar) were added. After charring for 10 minutes at room temperature, the tube was gently heated using an electrically-heated rack so that the acid refluxed well within the tube and the membrane was seen to break down. After 10 minutes, the solution was cooled and 2cm<sup>3</sup> of concentrated nitric acid (Analar) were added carefully with swirling. The solution was again refluxed until all traces of the membrane had disappeared (5-10 mins.) and then oxides of nitrogen were driven off by heating further for 1 to 2 minutes.

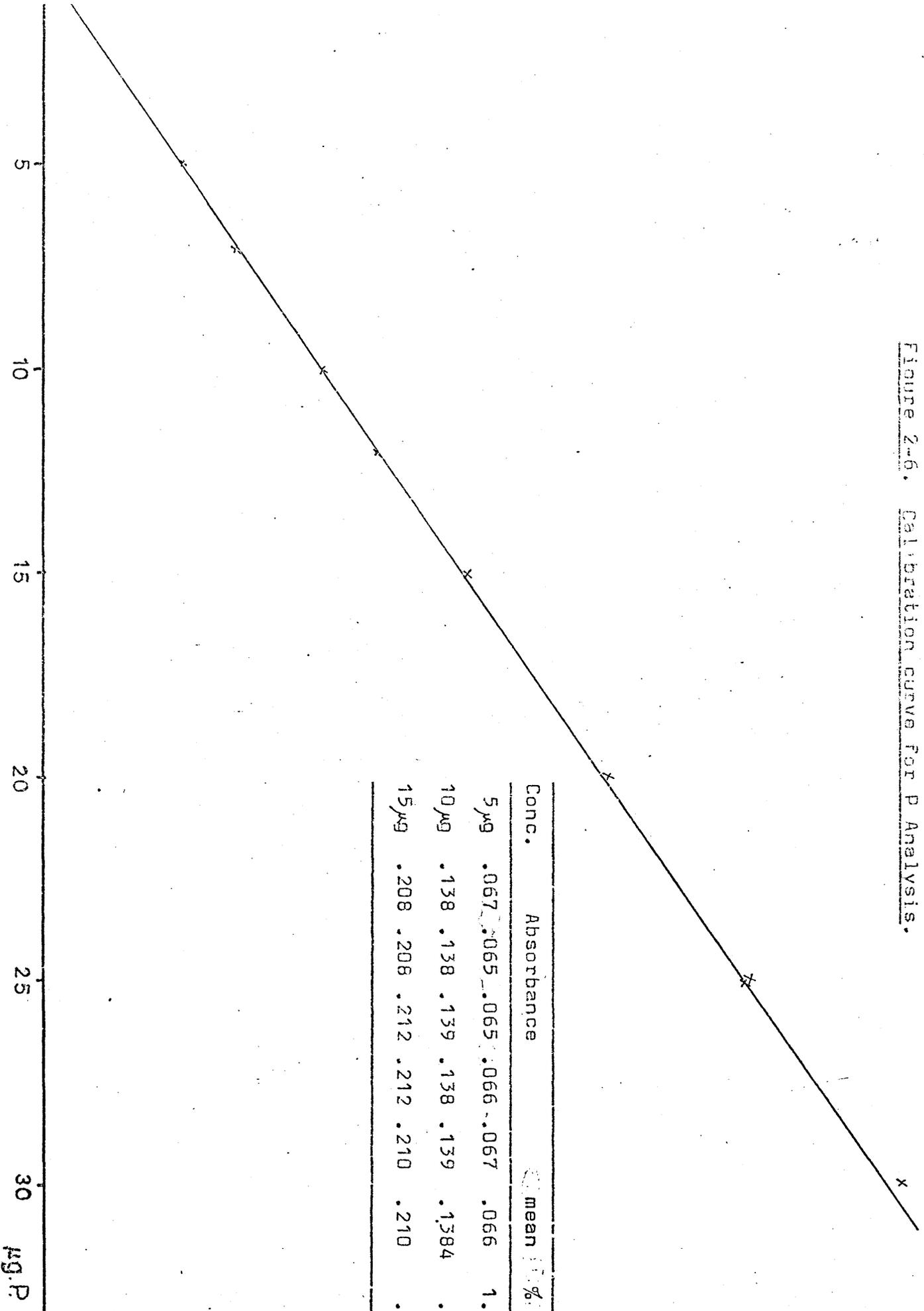
The clear, slightly yellow solution was allowed to cool then carefully diluted 1+1 with deionised water and reheated to expel remaining  $\text{NO}_x$ . During all the heating stages, the liquid was refluxed on the lower walls of the tube only. The final clear, almost colourless solution was allowed to cool then neutralised with 5M NaOH to phenolphthalein. Sufficient  $\text{H}_2\text{SO}_4$  was then added to discharge the phenolphthalein colour (this improved solution stability) and the solution was made up to  $50\text{cm}^3$  with distilled deionised water. Aliquots of this solution were then analysed using the following method:

An aliquot of solution containing not greater than  $25\mu\text{g}$  phosphorus (as P) was placed in a  $50\text{cm}^3$  volumetric flask and diluted to  $40\text{cm}^3$  with deionised distilled water. To this were added, with mixing,  $8\text{cm}^3$  of molybdate reducing agent. The volume was made up to  $50\text{cm}^3$  with water and the solution was thoroughly mixed. After 10 minutes, the absorbance of the blue solution was measured at 880nm using a spectrophotometer (SP600 Series 2, Pye Unicam Ltd., Cambridge, UK). A blank determination with  $40\text{cm}^3$  deionised water was made and the absorbance corrected for this, if necessary.

#### Solutions.

Ammonium molybdate solution;	40g tetrahydrate in 1l water
Ascorbic acid solution;	0.1 Molar solution in water. Made fresh daily.
Potassium antimonyl tartrate solution;	2.7g in 1l water.
5M Sulphuric acid;	$140\text{cm}^3$ conc. $\text{H}_2\text{SO}_4$ to 1l with water.

Figure 2-6. Calibration curve for P Analysis.



Conc.	Absorbance	mean	% RSD		
5 µg	.067	.065	.065	1.5	
10 µg	.138	.138	.139	.4	
15 µg	.208	.208	.212	.210	.95

Molybdate reducing agent;

Mix together 50cm<sup>3</sup> 5M H<sub>2</sub>SO<sub>4</sub>,  
15cm<sup>3</sup> ammonium molybdate  
solution and 30cm<sup>3</sup> ascorbic  
acid solution. Add 5cm<sup>3</sup>  
potassium antimonyl tartrate  
and mix well. This solution  
must be prepared daily and  
stored in a refrigerator when  
not in use. The above order of  
reagent addition must be  
adhered to.

Calibrations were constructed using solutions of potassium dihydrogen phosphate and the usable range was 0-30µg P. All reagents were of 'Analar' grade and it was found to be essential to use water of the highest purity (deionised-distilled) to minimise blanks. A typical calibration curve with the associated levels of precision is shown in Figure 2-6. Long term reproducibility of the calibration was excellent the relative standard deviation of a series of 10µg standards over an eight week period was around 1%.

## 2.4 Results and Discussion.

### 2.4.1 Solution casting.

Although a similar method to that employed in the production of PVC membranes was used,<sup>73</sup> in the case considered here, a chemical reaction was proceeding during solvent evaporation. This was found to cause some complications.

Firstly, it was found inconvenient to cast directly onto a glass plate. This was due to leakage of the polymer solution

under the glass ring and to the difficulty of removing the membrane after casting. The membranes which were formed showed much greater adhesion to glass than did PVC membranes and although it was possible to remove the glass after breaking it, this was both hazardous and costly. The use of a film on the glass plate was found necessary. This film being either a chemical releasing spray or an inert polymer film. In the first instance, few such sprays were available and it was thought likely that surface contamination of the membrane would occur through their use. On the other hand, few thin films are inert to THF although cellophane and Teflon were found to show adequate resistance. Cellophane was chosen due to its better ability to form a gasket seal between the glass surfaces, but the film had to be pure and uncoated. This film had to be stretched tight using embroidery rings in order to prevent shrinkage and wrinkling during membrane production. Membranes could usually be removed easily from the cellophane, any difficulty could be overcome by carefully wetting the cellophane and peeling it away from the membrane. The use of solvents other than THF was generally unsuccessful due to the occurrence of free radical quenching and transfer reactions. Toluene and 4-methylpentan-2-one were used, but obvious morphological changes occurred causing brittleness and evaporation times were very long.

It may be useful to outline the main requirements found for successful casting. In addition to the need for pure materials it was found necessary to dissolve the SBS (4g) in 50-60cm<sup>3</sup> THF for at least 24 hours. Any lower volume resulted in poor dispersion of the polymer with aggregation and shorter times did not yield true solutions. The exclusion of oxygen and moisture during casting was not found necessary. The pre-washing of the casting apparatus with THF, the high solvent volatility and the formation of a surface 'skin' all contributed to exclusion of such radical-quenching impurities.

The formation of a 'skin' and its preceding gel were useful for the above purpose, but tended to cause some complications during the later stages of the polymerisation. In particular, polymerisation from a gel to form a 'skin' was very rapid (due to an autoacceleration mechanism) and the top surface rapidly became solid. This skin decreased the power of the incident U.V. and the rate of solvent evaporation from the lower section of the membrane. This led to incomplete polymerisation of the lower layers of the cast particularly at lower ambient temperatures and when the lamp intensity was decreased with age. This lack of complete polymerisation was apparent from the opaque areas seen in many membranes caused by a two-phase polymer distribution. Several methods were used successfully to counter this effect.

- a) After 12 hours, the ring and membrane were placed in a vacuum oven at 1 torr and 50°C. 2 hours with the cellophane cover on and then 2-4 hours with the cover

off were sufficient to produce fully cross-linked, clear membranes.

- b) After 12 hours, the ring was inverted and U.V. shone onto what was the bottom face for 2 hours. The cellophane was then removed, the bottom face washed with a small quantity of THF and then the bottom face was irradiated for a further 2-4 hours. A clear, cross-linked film resulted. Membranes produced by this method did not generally exhibit a 'two sided' behaviour.
- c) With a very intense U.V. source, a cellophane cover with a small hole in its centre may be placed on the top of the glass ring in order to decrease the evaporation rate of the THF. This method resulted in a greatly increased reaction time (24 - 30 hours) and gave clear membranes. The use of intense U.V. for so long a period tended, however, to produce membranes showing some loss of elasticity due to high levels of degradative cross-linking.

Techniques a) and b) generally were used, b) giving the best results, although, as with all free radical initiated addition polymerisations, the final stages of polymerisation were the most difficult to control. The difficulties of exerting fine control over the polymerisation were great and it was this lack of control which led to the use of hot-pressing in the hope of producing polymer films with better reproducibility.

TABLE 2-1      Effect of membrane composition on physical properties.

<u>Membrane</u>	<u>TAP</u> <u>% m/m</u>	<u>ABIN</u> <u>% m/m</u>	<u>THF</u> <u>solubility</u>	<u>Physical properties</u> <u>of cast membranes</u>
A	2.5	0	sol.	Elastic, clear
B	5	2.5	insol.	Elastic, clear, sl. yellow
C	2.5	5	sl.sol.	Elastic, opaque
D	5	10	insol.	Clear with opaque inclusions
E	5	15	insol.	Bubbled, opaque inclusions
F	15	2.5	insol.	Elastic, clear, yellow
G	50	5	insol.	Oily, yellow, rigid
H	100	5	insol.	Thick, rigid with oily surface

#### 2.4.1.1 Physical properties.

Membranes produced by solvent casting were clear and colourless although islets of opacity were sometimes seen and a slight yellow coloration was often observed. Transmission and attenuated total reflectance (ATR) infra red (IR) spectroscopy was used to check the presence of P=O and P-O-Alkyl bands. Although such bands were visible, differences between the bands in free and bonded TAP were not discernible. Thus, use was made of other techniques to assess covalent incorporation of TAP.

It was known that cross-linked three-dimensional polymeric matrices were insoluble, so an assessment of membrane solubility would indicate the extent of cross-linking. Analysis of insoluble phosphorus in the membrane would indicate whether the cross-linking was by TAP and give the level of covalently-bound phosphate in the membrane.

Table 2-1 shows the effect on 'THF-solubility' of changing the levels of TAP and, or, ABIN. SBS itself was soluble when cast under U.V. light whilst low levels < 2%, TAP resulted in similarly soluble membranes although dissolution took comparatively longer. Higher levels of TAP yielded increasingly insoluble membranes showing a loss of elasticity. Large amounts of ABIN (e.g. membrane E) gave cross-linked, insoluble membranes whose physical properties were poor due to homo-crosslinking of the parent polymer in addition to cross-linking by TAP. The properties of membranes G and H indicated that high levels of

TABLE 2-2      Typical levels of phosphorus in membranes  
containing optimal TAP quantities (~5% m/m)

% P m/m		% covalently bound	% P m/m
As cast	THF insoluble		calc
.193	.073	37.8	.68
.200	.143	71.5	.602
.154	.035	22.7	.578
.14	.045	32	.606
.401	.121	30.2	.583
.279	.099	35.5	.58
.227	.094	41.4	.58
.319	.088	27.6	.602
Mean = <u>37.3%</u> .			

TAP or poly(TAP) itself yielded swollen, rigid membranes due to the very high levels of cross-linking seen with this trifunctional monomer. Optimal physical properties (insoluble membranes retaining some elasticity) were observed with low levels of TAP (2.5 to 10% m/m) in conjunction with half this amount of ABIN.

#### 2.4.1.2 Phosphorus Analysis.

Phosphorus analysis on several membranes (Table 2-2) indicated that not all the TAP was combined, some being lost by volatilisation during membrane production. In addition, not all of the P contained within the membrane was covalently bound as was indicated by the lower levels of THF - insoluble P. In practice, the THF-soluble P was washed out of the membrane during hydrolysis, so that levels of P in the final working membrane were much lower than would be calculated on the basis of initial reactants. On average, 37% of the P in the cast membrane was covalently bound i.e. 'THF-insoluble'. This further indicates the difficulties involved in reproducible casting when using free radical polymerisation and confirms that IR spectroscopy is unlikely to be able to indicate the environment around so many different P=O groups in such a complex matrix.

Many inter-related factors control the polymerisation throughout all its stages and the problems of precisely controlling this free radical polymerisation reaction are large. However, covalently-bound phosphate groups are generated at a fairly consistent level and the utility of the membranes formed depends ultimately upon their electrochemical performance.

## 2.4.2 Hot pressing.

The initial part of this program was in two parts, namely, to optimise pressing conditions and to assess methods of producing a homogeneous reaction mixture.

### 2.4.2.1 Pressing conditions.

It was essential to optimise the processing temperature so that adequate flow occurred in the press in the absence of thermal degradation. Values of the glass transition temperatures,  $t_g$  have been determined<sup>152</sup> for butadiene ( $t_g = - 81^{\circ}\text{C}$ ) and styrene ( $t_g = + 71^{\circ}\text{C}$ ) in SBS. SBS begins to soften at  $100^{\circ}\text{C}$  and industrial processing temperatures range from  $135^{\circ}\text{C}$  upwards.

In this study, SBS crumb was pressed at  $110^{\circ}\text{C}$  and 10 tons ram force and found to show very low flow. This flow increased with the applied temperature and at  $140^{\circ}\text{C}$  a polymer film with no flow lines was obtained. Further increases would have been to no advantage, as, with the purified and, therefore, less stable SBS being used, degradation would begin. At press temperatures of  $175\text{--}180^{\circ}\text{C}$  discolouration and degradation of the polymer began at the edges of the mould. Thus, a temperature of  $140^{\circ}\text{C}$  and a ram force of 10 tons were the conditions employed. In practice, the polymer and mould were placed in the press, which was already stabilised at  $140^{\circ}\text{C}$ , and the pressure steadily increased to allow spreading of the melting polymer. The reaction time was 5 or 10 minutes at full ram force (10 tons) and samples were cooled in air at ambient pressure.

#### 2.4.2.2 Reactant mixing.

Several methods were evaluated for this process (Sections 2.3.3.1 - 5), the major problem being one of mixing SBS (a solid) and TAP (a liquid). The use of mechanical mixing led to a non-homogeneous membrane and although this could be improved by increasing the reaction time, thermal degradation then became a problem. Solvent coating was also discarded as losses of TAP during solvent evaporation and on the flask walls were prohibitive. The pressing of a membrane which had been previously cast without U.V. irradiation did give rise to a homogeneous, cross-linked membrane, but this technique was not pursued as not only did this technique combine the worst volatility losses of both methods but it was also a lengthy process. Hot milling had been suggested as being the industrial method of choice for mixing rubbers and reactants. The combined effect of temperature and roller pinch should have resulted in the formation of a polymer paste into which the monomer and initiator may have been folded. The Micro-Mill was the only machine which could be found that would accept the small (<10g) sample quantities available, most machines tending to operate on the kilogram scale. Although giving favourable results with a silicone polymer, the mill was found to be useless for processing SBS. The primary reason for this was the low temperatures attainable with the heaters available (see temperature figures in Fig.2-5). These temperatures were not sufficiently high to give polymer flow and the effect of the

roller pinch at these bed temperatures was to cause cold shear of the polymer. This merely resulted in production of a finer crumb. In addition, if higher bed temperatures had been obtainable then the liquid TAP would have been volatilised. This would not only have resulted in a significant P loss, but would have created a significant hazard to anyone operating the mill. This technique, therefore, was abandoned for the TAP/SBS system, but it might prove to be the method of choice for other polymer/monomer combinations.

Lyophilysis was the most successful method of providing a homogeneous polymer reaction mixture. Difficulties were experienced with the technique, mainly in the control of solvent evaporation from a viscous polymer solution. The use of a small ball-bearing in the resin kettles was found indispensable for aiding nucleation in the bulk of the solution. Removal of the pre-polymer from the glass resin kettle was simple providing that good control of solvent evaporation had been maintained. Warming of the resin kettle in a heating mantle for a few seconds made removal of difficult specimens easy. Lyophilysis yielded an elastic prepolymer in a hemispherical shape which readily flowed in the press.

#### 2.4.2.3 Membrane properties.

The membranes produced by lyophilysis and hot pressing were of very even texture, slightly elastic and extremely tough. The P loss occurring in such membranes was investigated and some results are shown in Table 2-3 for a variety of TAP contents

TABLE 2-3    Phosphorus distribution in lyophilised and pressed membranes

MEMBRANE	TAP (% <sup>w</sup> /w)	%P		
		LYOPHOLISED	PRESSED	CALCULATED
LP 11	0	$7.3 \times 10^{-4}$	—	zero/blank
LP 12	0.129	.021	—	.018
LP 13	.588	.077	.056	.083
LP 14	.973	.104	.047	.138
LP 15	2.48	.35	.35 <sup>c</sup> .35 <sup>e</sup>	.35
LP 16	5.06	.66	.617 <sup>c</sup> .59 <sup>e</sup>	.718
LP 17	10.0	1.32	1.206 <sup>c</sup> 1.07 <sup>e</sup>	1.42

c- sample from centre of membrane.

e-    "        "    edge    "        "

Pressing conditions - no initiator.

- 140<sup>o</sup>C .

- 10 tons ram force.

- 5 mins.

under the conditions specified. Losses of TAP were low and homogeneous on lyophilysis although as the TAP level was increased so, proportionately, was the loss of P. As might have been expected, the P losses experienced on pressing at 140°C were significant and again became worse as the TAP content was increased. More significantly, however, the P losses across the membrane were not homogeneous - as indicated by membranes LP 15, 16 and 17. In this series, the loss became worse at the edge of the pressed sample. This was consistent with increased TAP volatility out of the edge of the press mould. Not only did this produce a membrane with a non-homogeneous P distribution, but it also formed a hazard during press operations. Despite this, the physical properties were, seemingly, more controllable and reproducible than when casting. A true evaluation of the utility of lyophilysis and hot pressing for the production of SBS/TAP membranes would depend on their electrochemical properties.

Thus, it has been demonstrated that polymeric matrices containing covalently bound phosphate groups can be prepared. When using TAP, hydrolysis of these membranes is necessary in order to produce the required exchanger group. The effect of the conditions of this hydrolysis are considered in the next chapter as the effect of hydrolysis on physical properties is not great compared to its effect on electrochemical properties.

## 2.5 Conclusions.

Many methods of producing membranes from SBS and TAP have been investigated. There were many difficulties encountered in the production of an addition polymer by free-radical initiation using the techniques available. The two most favoured techniques for the production of membranes with covalently-bound phosphate sensor groups and appropriate physical properties were solution casting and lyophilysis/hot pressing. Neither of these methods was capable of producing perfectly reproducible membranes with no loss of TAP monomer. However, both techniques yielded membranes cross-linked by the organophosphate monomer.

It is the electrochemical evaluation of the resulting membranes that will indicate which of the two methods of production (if any) can be used for fabricating calcium ISE membranes. It is this evaluation which is described in the next chapter.

CHAPTER 3

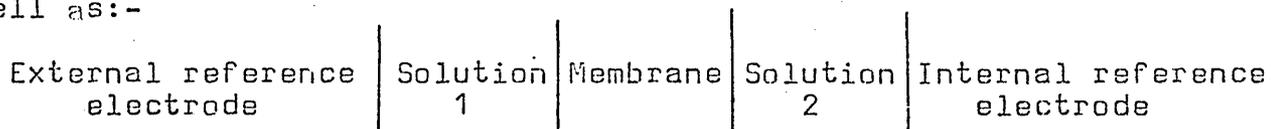
ELECTROCHEMICAL PROPERTIES OF  
COVALENTLY BOUND SENSOR MEMBRANES.

### 3.1 Theoretical principles of ion-selective electrode response.

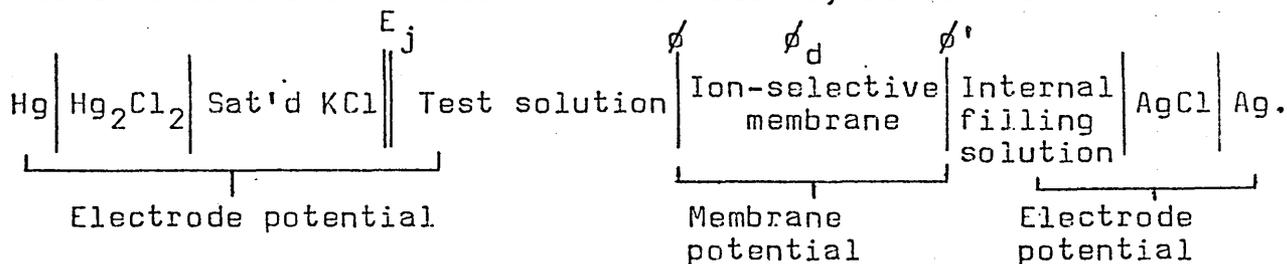
The theoretical basis of ion selective electrodes is now well-advanced for many types of electrode. It is not the intention of this writer to cover theoretical detail exhaustively as in-depth accounts may be consulted in books<sup>153,154,155,156</sup> and a biannual review<sup>157</sup>. However, sufficient background theory is supplied to enable understanding and appreciation of the electrochemical properties of the membranes which have been produced.

#### 3.1.1 The Nernst Equation.

We may visualise an ion selective electrode measurement cell as:-



and, if, as is often the case, the external reference is a calomel electrode and the internal reference element is a silver-silver chloride electrode then the cell may be written:-



$E_{ref}$

$E_m$

$E'_{ref}$

$$E_m = \Delta\phi = \phi + \phi_d - \phi' \quad (3-1)$$

The overall observed potential of this cell is made up of potential contributions from the reference elements, the membrane and any liquid junctions present such that;

$$E_{\text{cell}} = E_{\text{ref}} + E_j + E_m - E'_{\text{ref}} \quad (3-2)$$

In practice, the two reference potentials are maintained constant by the respective filling solutions and consistency of the liquid junction,  $E_j$  is assumed. Thus, any change in the overall cell potential,  $E_{\text{cell}}$  brought about by changes in the test solution are usually assumed to arise from changes in the membrane potential,  $E_m$ . This membrane potential,  $E_m$  is determined by the potentials developed at the two membrane-solution interfaces ( $\phi$  and  $\phi'$  in equation 3-1) and by the membrane diffusion potential,  $\phi_d$ . One of the interfacial potentials,  $\phi'$  is maintained at a constant level by the internal reference solution and  $\phi_d$  is assumed constant for any particular membrane. Thus,  $E_m$ , the overall membrane potential and thereby,  $E_{\text{cell}}$ , will be determined only by the change in the 'outer' membrane potential,  $\phi$  brought about by the changing activity of the determinand ion in the test solution.

The Nernst equation (3-3) relates the overall cell potential of a membrane electrode to the activity of the determinand ion ( $a_i$ ) in contact with the outer boundary of the ion-selective membrane

$$E = E^0 + \frac{2.303 RT}{z_i F} \log_{10} a_i \quad (3-3)$$

The term  $E^0$  incorporates the electrode potentials  $E_{ref}$ ,  $E'_{ref}$  and  $E_j$ ,  $R$  is the gas constant,  $T$  the absolute temperature and  $F$ , the Faraday.  $a_i$  is the activity of the determinand ion of charge  $z_i$ .

The essential feature of the Nernst relationship when applied to calcium ISE is that a calibration of  $E$  vs  $\log_{10} a_i$  can be expected to show a slope,  $S = + \frac{2.303 RT}{z_i F} = + 29.6\text{mV}$  per decade change of  $a_{Ca^{2+}}$  at  $25^\circ\text{C}$ . This slope is often known as the Nernstian slope and, whilst many ISE show such a calibration slope exactly, most ISE calibrations are seen to be within  $\pm 2\text{mV}$  of the 'ideal' value.

Figure 3-1 shows a typical calibration curve for a calcium ISE with a Nernstian slope of  $+ 29.6\text{mV}\cdot\text{decade}^{-1}$  and a wide linear working range. The upper activity level may be limited by the number of ion-exchange sites available within or on the membrane. The lower activity limit may be governed by the solubility of the sensor material and the equilibrium ion exchange constant in the test solution or by the difficulty of removing (interfering) trace ions from solution. The limit of detection (lod) may be determined from such a calibration by either of two methods.<sup>158,159</sup>

- a) if the calibration consists of two linear sections, then extrapolation of these linear portions indicates the point at which the electrode begins to respond - the l.o.d. (see Fig.3-1a).

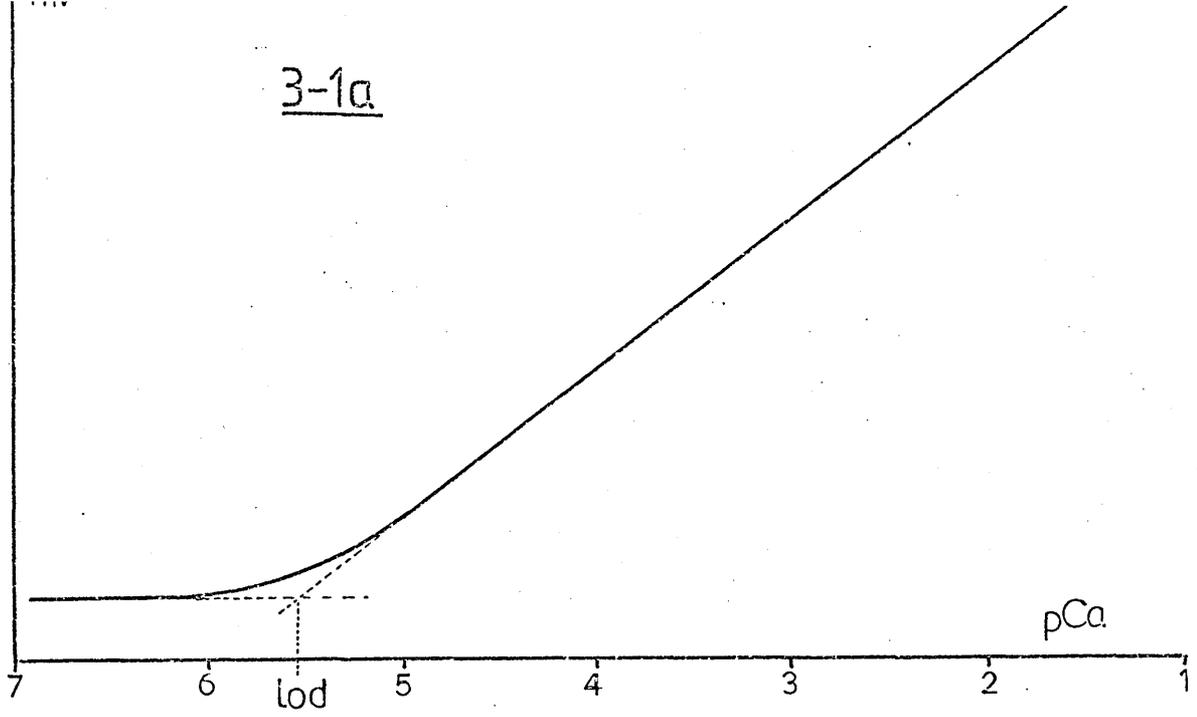
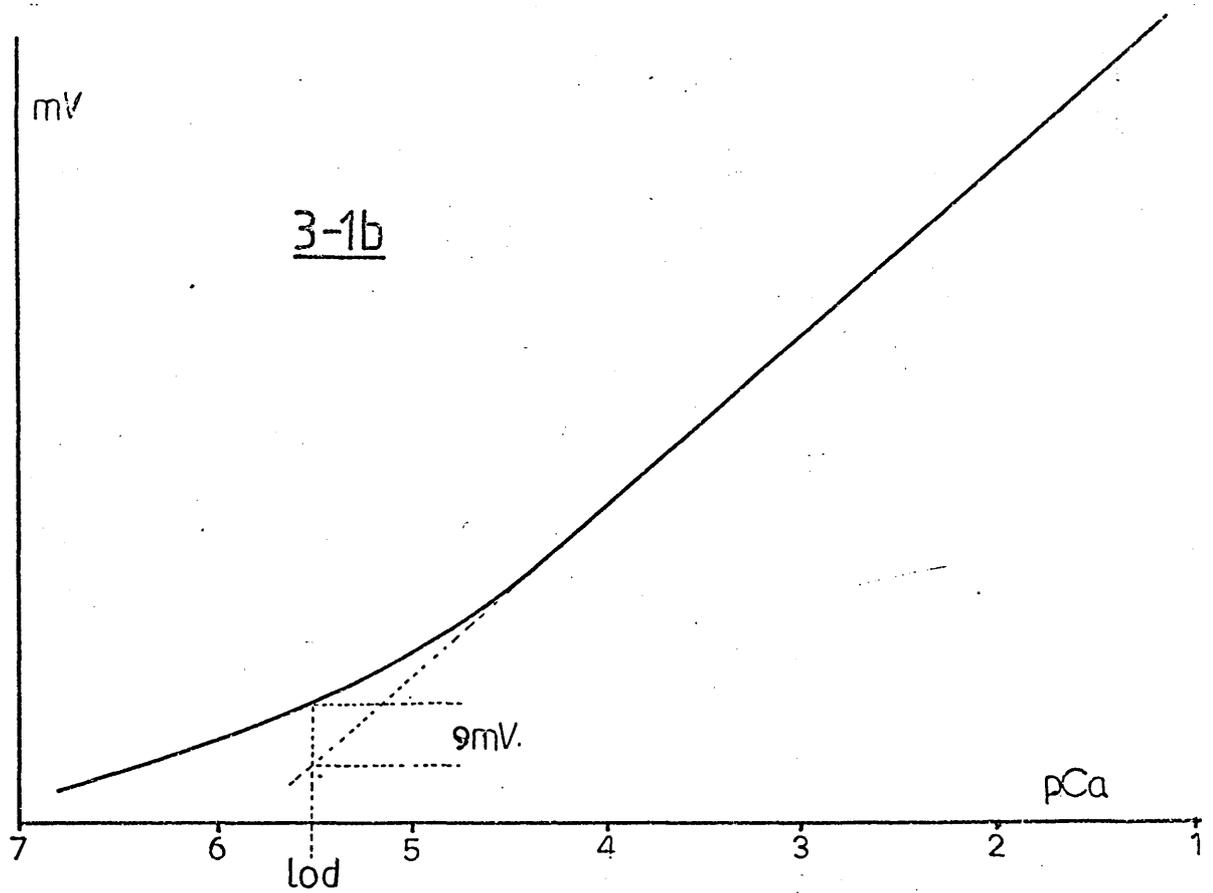


Figure 3-1. Calibration curve for a calcium ISE showing l.o.d. determination from;  
 a) linear extrapolation,  
 b)  $18/z$  deviation.



b) if the calibration is a linear portion followed by a curved section as shown in Fig.3-1b, then a method similar to one used for selectivity coefficient determination may be used. (See Section 3.1.3.1, Method 2). This involves finding the point at which the actual curve differs from the extrapolated line by  $18/z$  mV.

### 3.1.2 Activity and Activity Coefficients.

The potentials arising at permselective membranes are related to the logarithm of the activity of determinand ions rather than to their total concentration. The activity of an ion in solution may be simply related to its concentration by the equation;

$$a_i = C_i \gamma \quad (3-4)$$

where  $\gamma$  is the activity coefficient. This activity coefficient depends upon all the ions in solution and has been related to the total ionic strength,  $I$ , where;

$$I = \frac{1}{2} \sum C_i z_i^2 \quad \text{where } C = \text{concn. in mol.l}^{-1} \\ z = \text{ionic charge} \quad (3-5)$$

by the Debye-Hückel equation;

$$\log \gamma = -Az^2 I^{1/2} \quad (3-6)$$

$A$  is a constant dependent on solvent and temperature ( $A = 0.511$  at  $25^\circ\text{C}$  for water). The Debye-Hückel equation is strictly only applicable at or near infinite dilution (zero concentration) where  $\gamma \approx 1$ , but has been used to predict  $\gamma$  values up to 0.1 molar. As the concentration increases from  $10^{-4}\text{M}$  to  $10^{-1}\text{M}$ , the value of  $\gamma$  decreases as the ionic strength

increases. Several empirical extensions of equation 3-6 have been used to fit the observed deviation from the predicted values at and above  $10^{-1}$  Molar. No attempt will be made here to enter into the theoretical implication of using any one particular equation to calculate  $\gamma$ , or to comment upon the use of single ion activity coefficients. For further discussion of this topic, reference may be made to other publications on the subject.<sup>160,161</sup> The extension of the Debye-Hückel equation used throughout this work to calculate values was;

$$\log \gamma_{\text{Ca}^{2+}} = -z^2 \left[ \frac{A I^{1/2}}{1 + I^{1/2}} - 0.2 I \right] \quad (3-7)$$

which has been used extensively in similar studies by researchers at UWIST and found to give an adequate fit to the observed behaviour. Similarly, use of the convention

$$p_{\text{Ca}} = -\log a_{\text{Ca}^{2+}}$$

has been made and is used here without further comment.

### 3.1.3 Selectivity and Selectivity Coefficients.

No electrode has total specificity for one ion in the presence of all other ions. Thus, electrodes are described as being selective in so far as they will favour response to the primary ion in the presence of other (interfering) ions. It is therefore necessary to modify the Nernst equation (3-3) in order to account for the response of an electrode to ions other than the one of major interest.

For an ion selective electrode responsive to a primary ion,  $i$ , the potential response is modified in the presence of an interfering ion,  $j$ , such that;

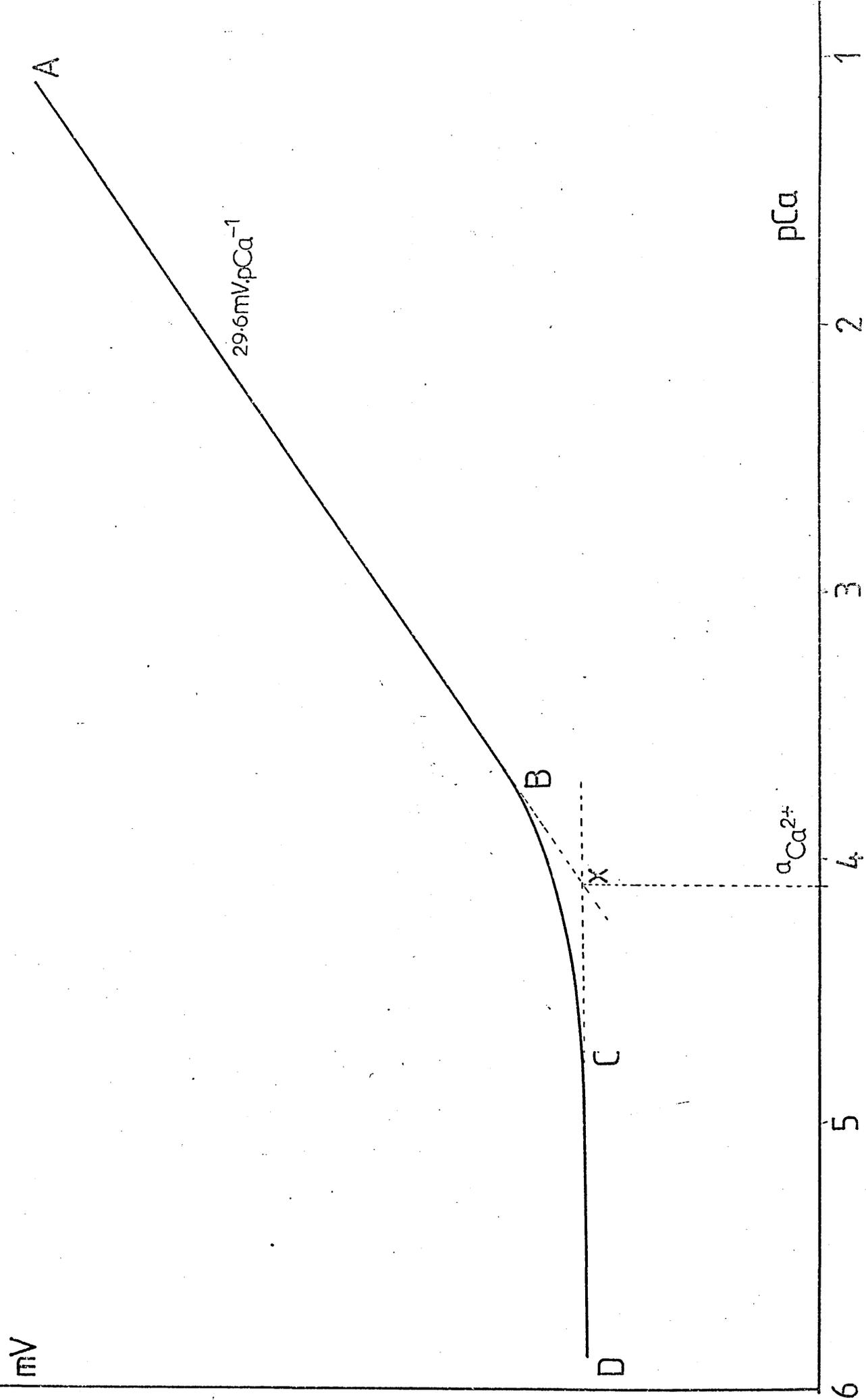
$$E = E_0 + \frac{2.303 RT}{z_i F} \log_{10} \left[ a_i + k_{ij}^{\text{pot}} a_j^{z_i/z_j} \right] \quad (3-8)$$

where  $k_{ij}^{\text{pot}}$ , the potentiometric selectivity coefficient, is a measure of the degree of selectivity shown by the electrode for ion  $i$  in the presence of ion  $j$ . The value of this coefficient varies with  $a_i$  and  $a_j$  and there are two commonly used methods for the numerical evaluation of selectivity coefficients.

### 3.1.3.1 Mixed solution or fixed interference method.

This technique is the one of preference and widest use. It depends upon the measurement of electrode response to the primary ion in the presence of a fixed background level of an interfering ion. In practice the primary ion activity,  $a_i$ , is changed in the presence of a constant background of the interfering ion,  $a_j$ . This data is plotted as a calibration curve e.g. Figure 3-2, which shows the effect of a background interferent ( $10^{-3} \text{ M Mg}^{2+}$ ) upon the response of a calcium ISE. Two linear regions exist in this graph, AB and CD. The first linear region (A-B) shows a Nernstian response to calcium ion whilst the second (C-D) shows the limiting potential caused by the background level of magnesium ions. Below about  $10^{-4} \text{ M Ca}^{2+}$  the electrode is unable to detect changes in  $a_{\text{Ca}^{2+}}$  due to the presence of the  $\text{Mg}^{2+}$  ions. The intermediate section of the graph (B-C)

Figure 3--2 Calibration curve for a calcium ISE in the presence of an interfering ion,  $Mg^{2+}$



is a curve where the electrode response to the primary ion is being increasingly overwhelmed by the response to the interfering ion. In order to determine the selectivity coefficient,  $k_{CaMg}^{pot}$ , from the graph three methods are available. The first two methods are, in fact, special cases of the limit of detection (lod) determination where the lod is determined by the presence of the interferent ion.

#### Method 1

Providing AB and CD are straight lines (as in Fig.3-1a) then the intersection of the extrapolations of these two lines at point x indicates the point at which the electrode responds equally to both ions and, it can be shown (from equation 3-8);

$$k_{CaMg}^{pot} = \frac{a_{Ca}^{z_{Mg}}}{a_{Mg}^{z_{Ca}}} \quad (3-9)$$

where  $a_{Mg}$  is the known background interferent level and  $a_{Ca}$  is the calcium ion activity corresponding to point x.

#### Method 2

If C-D is curved (as in Fig.3-1b), then it may be stated that both ions are contributing equally to the observed electrode potential when;

$$a_{Ca} = k_{CaMg}^{pot} a_{Mg}^{z_{Ca}/z_{Mg}} \quad (3-10)$$

As  $z_{Ca} = z_{Mg} = 2$ , equation 3-8 becomes;

$$E = E^0 + \frac{2.303 RT}{2F} \log_{10} \left[ a_{Ca} + k_{CaMg}^{pot} a_{Mg} \right] \quad (3-11)$$

Combination of equations 3-10 and 3-11 yields;

$$E = E^0 + \frac{2.303 RT}{2F} \log_{10} (2a_{Ca}). \quad (3-12)$$

Now the difference between the electrode potential in a solution of pure calcium ions (equation 3-3,  $i = Ca$ ) and that in a solution of calcium ions with a background of magnesium ions,

$a_{Mg}$  is;

$$E = \frac{2.303 RT}{2F} (\log_{10} 2a_{Ca} - \log_{10} a_{Ca}) \quad (3-13)$$

$$= \frac{2.303 RT}{2F} \log_{10} 2$$

$$= 8.9 \text{ mV at } 25^{\circ}\text{C.}$$

Thus, the point at which the calibration curve for  $Ca^{2+}$  in the presence of a constant background of  $Mg^{2+}$  differs from the extrapolation of the Nernstian portion (A-B) by 8.9 mV.

corresponds to  $a_{Ca}$  and,

$$k_{CaMg}^{pot} = \frac{a_{Ca}}{a_{Mg}} \quad (3-14)$$

### Method 3

This method, developed by Srinivasan and Rechnitz<sup>163</sup> involves the linearisation of equation 3-8. However, the variation of  $k_{ij}^{pot}$  values with  $a_i$  and  $a_j$  and the generally wide range of  $k_{ij}^{pot}$  values seen for ISE mean that any advantage to be gained from a lengthy mathematical treatment is lost.

### 3.1.3.2 Separate solution method.

The use of separate solution determinations of  $k^{\text{pot}}$  values is not generally recommended as, in a 'real life' analytical sample, one would seldom be required to measure interferent in the absence of determinand. Despite this, the method has been, and still is, used by some workers. The IUPAC recommendation<sup>158</sup> for this method is to measure and compare the potential of the ISE/reference electrode cell, first in pure determinand,  $i$ , and then in pure interferent,  $j$ . If  $a_i = a_j$  (the isoconcentration method) then the potentiometric selectivity coefficient,  $k_{ij}^{\text{pot}}$  may be calculated from the observed potentials,  $E_i$  and  $E_j$ ;

$$\log k_{ij}^{\text{pot}} = \frac{E_j - E_i}{2.303 RT/z_i F} + \left(1 - \frac{z_i}{z_j}\right) \log a_i \quad (3-15)$$

By whichever method the values of  $k^{\text{pot}}$  are determined care should be exercised in their presentation and interpretation. Firstly, the equation used for selectivity coefficient determination, (equation 3-8) is an empirical one fitting observed data. Secondly, the power term in equation 3-8 may add confusion if  $z_i \neq z_j$  and it must also be remembered that the value of  $k_{ij}^{\text{pot}}$  depends upon the activity of the interfering ion,  $a_j$ . Consequently, when quoting selectivity data, conditions of their measurement should be clearly stated and if space permits, the use of selectivity plots such as Fig.3-2 is advantageous. This would give a graphical impression of the working range of an ISE in the presence of projected levels of interfering ions. Alternatively, maximum levels of interferent

tolerable may be used, but this depends upon the activity of the primary ion.

#### 3.1.4 Response times.

The response time of an ISE depends upon factors such as the mechanism of response, temperature, electrode pretreatment, stirring rate, activity of primary and interferent ions etc. A static response time indicates the time taken for an electrode set to assume an equilibrium potential when placed in a fresh solution. More realistically, the dynamic response time may be determined as the time taken for the electrode to reach an equilibrium potential (or an arbitrary proportion of the change) after a step change in determinand activity. As with  $k^{pot}$  values, the conditions of measurement must be stated to give a meaningful result. Use of a  $t_{95}$  response time value i.e. the time taken to reach 95% of the equilibrium potential value, has been made<sup>162</sup> although recent recommendations from IUPAC<sup>159</sup> favour a  $t_{90}$  response time.

#### 3.1.5 General Analytical Performance.

In common with most analytical techniques, day to day and run to run drift occurs. The measurement of this is simple with ISE, but as with other measurements, many factors control both drift and precision and these should be stated alongside quoted figures. Although it is generally essential to minimise or eliminate the effects of temperature change in order to produce optimum analytical performance, it is also useful to study the effect of temperature change on ISE response. In

particular, the working temperature range and the effect of temperature on slope and response time might usefully be determined.

It is worth noting that because the potential varies linearly with the logarithm of the determinand activity, then precision is limited with ISE. Thus, a 10% increase in  $a_{Ca^{2+}}$  only yields a 1.23 mV potential change. However, this precision is maintained throughout the electrode range and the drawback of limited precision is to an extent compensated for by the generally wide range of electrode response.

## 3.2 Experimental

### 3.2.1 Hydrolysis.

Hydrolysis was generally carried out under reflux. Reagent grade NaOH, KOH and methanol were used as received. Any hydrolyses carried out using  $Ca(OH)_2$  were under nitrogen in order to exclude  $CO_2$  from the apparatus. Sections of membranes were hydrolysed rather than discs to ease identification of several membrane fragments hydrolysed simultaneously.

After the required period of hydrolysis, the membranes were washed in hot deionised distilled water and dried. The resulting membrane sections were then ready for mounting either immediately or at any later time.

### 3.2.2 Ion selective electrode construction.

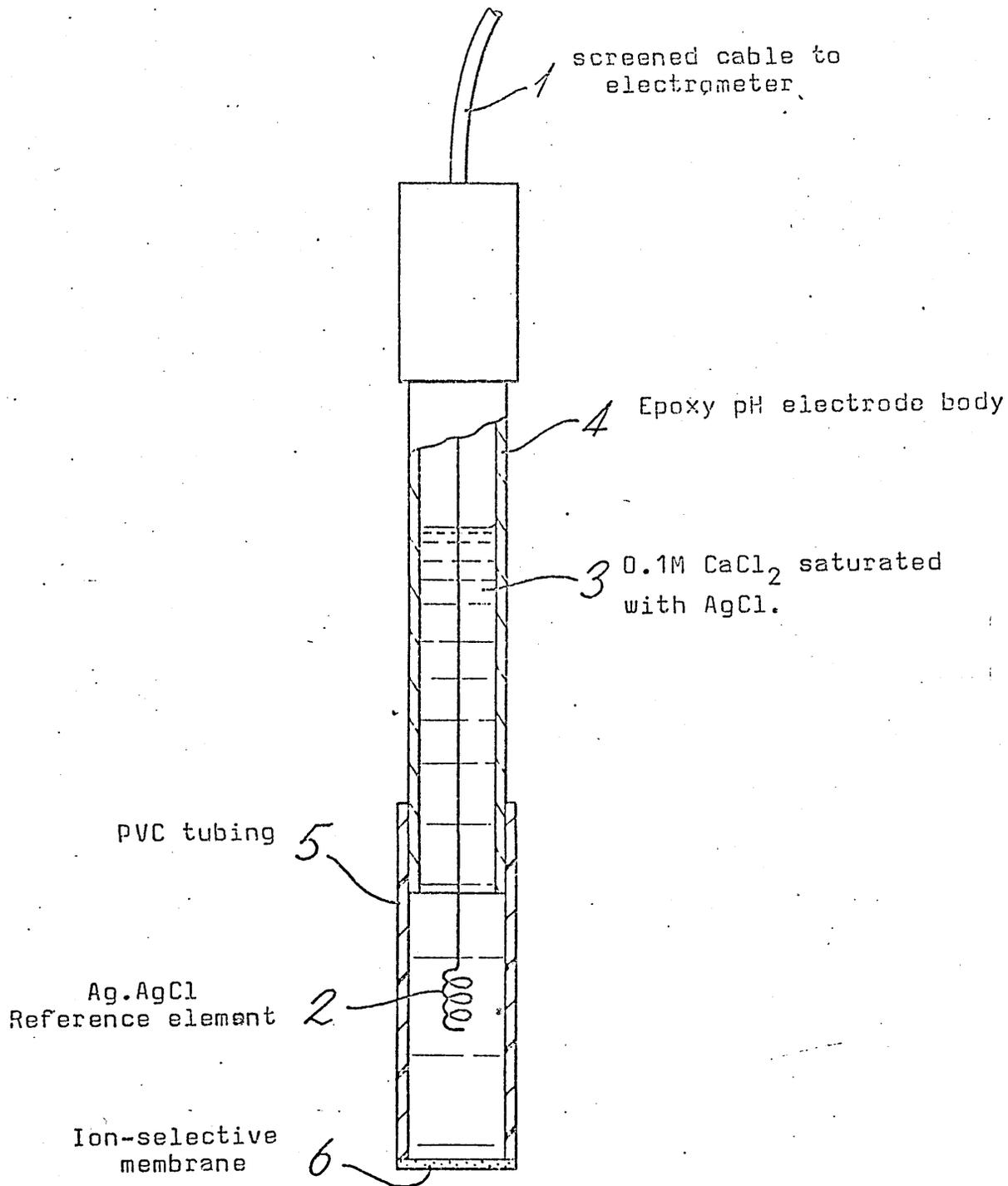
Discs of hydrolysed ion exchange membrane were cut with a cork borer (9mm dia.) and stuck to the polished end

of a 5cm. long section of clear, plasticised PVC tubing (9mm o.d., 6mm bore) with a cyanoacrylate adhesive (1S 496, previously 1S 12, Loctite Ltd., Dublin, Eire). The glue line was sealed with Loctite Water Proofing Solution to prevent deterioration of the seal. The mount was then left in air for at least two hours to allow complete curing. Difficulties were sometimes experienced with gluing and the use of Activator NF (Loctite) was found useful. In the absence of the commercial glue sealer, a solution of PVC in THF was used.

The resulting sensor unit was conditioned in a solution containing calcium ions and then incorporated into a modified, epoxy-bodied pH electrode as shown in Figure 3-2.2. The only modifications necessary were to shorten the epoxy body (4), remove the pH sensitive glass bulb and coil the silver-silver chloride reference element (2). The sensor unit (5,6) was attached to the epoxy body by either push-fitting or paraffin film. The use of this approach made the sensor units rapidly interchangeable and internal reference solutions could be simply replaced. In addition, few pH bodies were required and expense was kept to a minimum.

The commercially-available Orion 92-20 Calcium ISE (Orion Research Inc.) was used which was assembled as described in the manufacturers' instruction manual.

Figure 3-2.2 Ion-selective electrode with covalently-bound sensor group membrane.



### 3.2.3 Reference electrodes.

Two types of reference electrodes were used during this study;

- a) a saturated calomel single junction reference electrode. (Orion 91-01, Orion Research Inc., 11 Blackstone Str., Cambridge, Mass. 02139. USA.);  
or (Corning 476002, Corning Medical, Halstead, Essex, UK).
- b) double junction silver-silver chloride electrode (Corning 47606700M superceded by 0028102, Corning Medical) containing an inner solution of 4M KCl and a bridge solution of 1M  $\text{KNO}_3$ .

### 3.2.4 Meters.

Potential measurements were made with two meters:

Orion 701 (Orion Res.Inc., Cambridge, Mass., USA);  
Philips PW 9409 (Philips, Pye Unicam, York St., Cambridge, UK),

both meters had an input impedance  $>10^{12}\Omega$  and were capable of a precision of  $\pm 0.1$  mV.

pH measurements were made with a Pye 290 Expanded Scale pH meter (Pye Unicam, Cambridge, UK).

### 3.2.5 Ancillary Equipment.

All potential measurements were made at  $25 \pm 0.5$  °C unless otherwise stated. Distilled-deionised water used was at this temperature. When measurements were taken, the test solution ( $100\text{cm}^3$ ) was held in a  $150\text{cm}^3$  Pyrex beaker inside a copper coil encased in polystyrene. Water was pumped through

the copper coil at a temperature sufficient to minimise heat loss from the test solution allowing the latter to remain at 25°C for long periods. Stirring was accomplished magnetically at 250 rpm (Grant MS 1, Grant Instruments, Cambridge, UK) with Teflon-coated magnetic stirrer bars.

### 3.2.6 Calibration technique.

Calibrations were established either by serial dilution of a concentrated calcium chloride standard (Molar CaCl<sub>2</sub>, 'AVS' solution, BDH, Poole, Dorset) or by 'spiking' deionised water with small aliquots of concentrated standards. In the spiking technique, aliquots of 0.1 or 1 M CaCl<sub>2</sub> standards were added to deionised and distilled water to cover the range 10<sup>-6</sup> to 2x10<sup>-2</sup> M Ca<sup>2+</sup>. Microlitre quantities were added by means of either a steel in glass syringe (SGE Pty., Melbourne, Australia) or an adjustable micropipette (Oxford Sampler II 5-50 μl micropipette, Oxford Instruments, Athy, Co.Kildare, Ireland). Larger volumes were dispensed by Rocket piston syringe.

The use of such a 'spiking' technique was found to be advantageous when screening many electrodes for response. It enabled the rapid calibration of electrodes in either pure calcium or calcium + interferent solutions with a clean solution for each calibration. The technique also gave great flexibility for expanding any or all of the electrode range and also supplied a measure of dynamic response time without modification.

Caution must be observed when working at or below  $10^{-5}$  M as at these dilutions, the use of unbuffered solutions may result in problems as with any other trace analytical technique.

Calibration curves were constructed of potential vs.  $\log_{10}$  (activity). Activity coefficients were computed using the BASIC program ION in Appendix 1. The use of pure solutions and activity corrections was made throughout this study as the use of complexing agents and ionic strength buffers would merely have served to complicate potential responses during early development of an ion selective electrode.

### 3.2.7 Resistance measurements.

D.c. resistance measurements were made on the cell:-

Reference electrode || test solution | membrane | Reference  
Electrode

using a Keithley Instruments 610 c solid state electrometer (Keithley Instruments, GmbH, Munich, W.Germany). The test solution was  $10^{-3}$  M  $\text{CaCl}_2$  at  $25^\circ\text{C}$ . A standard resistor ( $2.2 \times 10^9 \Omega$ ) was used to check accuracy and drift of the meter.

### 3.3 Results and Discussion

#### 3.3.1 Conditioning of membranes.

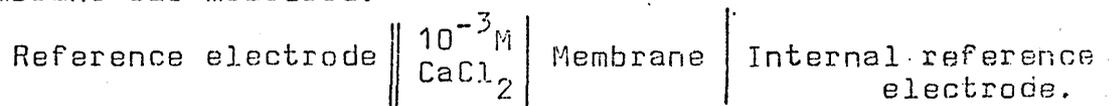
Having produced a membrane containing covalently-bound phosphate groups by either solvent casting or hot-pressing it was at first necessary to hydrolyse these membranes. Under the alkaline conditions employed for hydrolysis (aqueous or methanolic NaOH or KOH) a dialkylphosphate exchange group was formed. This group existed as the Na or K form of the exchanger and in order to generate the required Ca form it was necessary to condition the membrane. This was accomplished by placing the membrane in a solution containing  $\text{Ca}^{2+}$  ions which displaced the  $\text{Na}^+$  or  $\text{K}^+$  ions. The efficacy of conditioning in calcium chloride solutions in the range  $10^{-3}$  to  $10^{-1}\text{M}$  was found to be independent of the concentration. The length of time of conditioning required to give a full response depended upon the recent history of the membrane. For instance, if the membrane was conditioned immediately after aqueous hydrolysis then 8 hours were sufficient. However, if the membrane was allowed to dry out after hydrolysis then periods of 24 hours were often required for full conditioning. This indicated that not only was the conditioning process necessary for the production of the Ca form of the exchanger, but it was also needed for the response mechanism to function.

It appeared that the membrane must take up some water for the response to develop. This was qualitatively indicated by the slight opacity which developed in the membrane phase.

TABLE 3-1. Resistance (d.c.) of various cell sets.

Electrochemical cell			Resistance
	Body	Reference	/ohms
76e	A	Ag.AgCl	$4.3 \times 10^6$
			$4.4 \times 10^6$
	B	AgAgCl	$4.3 \times 10^6$
	A	Calomel	$4.5 \times 10^6$
	B	Calomel	$4.4 \times 10^6$
-----			
Orion	92 - 20	Ag.AgCl	$5 \times 10^7$
	Calomel	Ag.AgCl	$3.6 \times 10^5$
	74q with no int.ref. solution		$1.7 \times 10^{11}$
	Air		$6 \times 10^{13}$

The difficulty of measuring this water uptake led to the use of membrane resistance as a less empirical indication of membrane conditioning. The measurement of the resistance of polymeric films is generally difficult due to their insulating properties. Attempts to measure the resistance of the dry parent membranes met with no success. This was to have been expected as SBS was a rubber and should have exhibited insulating properties whose measurement requires the use of sophisticated and well-shielded equipment. As no such equipment was available, the resistance of an electrode cell containing the membrane was measured:



Using a functional electrode (76e) mounted on either of two bodies in conjunction with either of two reference electrodes, the results shown in Table 3-1 were obtained. These results indicated that the resistance of the cell set was unaffected by the body on which the membrane sensor unit was mounted. The reference electrodes gave rise to a slight bias so readings were all taken with the silver-silver chloride reference electrode. The upper limit of useful resistance measurement was indicated in the extreme case by air ( $10^{13} \Omega$ ) and by the resistance of an electrode containing no internal filling solution ( $1.7 \times 10^{11} \Omega$ ). The lower limit was set by the resistance of the reference electrode with its liquid junction and the value of  $3.6 \times 10^5 \Omega$  for a freely-conducting system was found to be

TABLE 3-2 Effect of conditioning on membrane resistance.

Electrode	Time elapsed, (hrs)			Comments	
	0	6	17	29	43
73	$6 \times 10^{10}$	$3.7 \times 10^{10}$	$6 \times 10^{10}$	$8.7 \times 10^{10}$	$8.5 \times 10^{10}$
75c	$5 \times 10^{10}$	$2.8 \times 10^9$	$2.75 \times 10^7$	$6.6 \times 10^6$	$4.5 \times 10^6$
75d	$4.8 \times 10^{10}$	$1.4 \times 10^{10}$	$4.6 \times 10^7$	$8.3 \times 10^6$	$4.35 \times 10^6$
Electrode	Time elapsed, (hrs)				
	0	4	9	23	
74q	$4.8 \times 10^{10}$	$3.4 \times 10^{10}$	$6.2 \times 10^8$	$7.1 \times 10^6$	
74r	$2.8 \times 10^{10}$	$3.6 \times 10^8$	$1.15 \times 10^8$	$3.1 \times 10^7$	
74s	$2.5 \times 10^{10}$	$1.6 \times 10^9$	$6.5 \times 10^8$	$1.87 \times 10^8$	
74t	$2.85 \times 10^{10}$	$4.3 \times 10^8$	$1.5 \times 10^8$	$3.8 \times 10^7$	
75d <sub>2</sub>	$2.95 \times 10^{10}$	$3.2 \times 10^7$	$6.8 \times 10^6$	$2.5 \times 10^6$	
75e	$5.7 \times 10^{10}$	$1.4 \times 10^7$	$7.2 \times 10^6$	$4 \times 10^6$	
78g	$1.9 \times 10^6$	$5.8 \times 10^5$	$4.5 \times 10^5$	$4.5 \times 10^5$	Anionic

noisy response

limiting. Thus, it may be assumed that any measured resistance of the cell-set lying between the above two limits is due to the resistance of the membrane. The measurement of the resistance (d.c.) of the cell-set would, therefore, directly reflect the resistance of the incorporated membrane.

On the basis of the above assumption, electrodes were prepared and the change in d.c. resistance upon conditioning in a solution ( $10^{-3}$  M in  $\text{CaCl}_2$  and  $10^{-3}$  M HCl) at  $20^\circ\text{C}$  was monitored. The results from this study are presented in Table 3-2. A pure SBS membrane acted as an insulator even after extended soaking. On the other hand, membranes containing 4.5% TAP and hydrolysed in methanolic KOH (75c - 75e inclusively) showed a steady fall of resistance with time until a value in the 1-10  $\text{M}\Omega$  range was reached. This resistance was characteristic of stable, responsive electrodes. Membrane 74s had a slightly high resistance ( $187\text{M}\Omega$ ) and exhibited a response prone to electrostatic interference, whilst an electrode exhibiting an anionic response (78g) showed an initial resistance of  $1.9\text{M}\Omega$  decreasing to  $4.5 \times 10^5 \Omega$  indicating a freely-conducting, porous membrane. Thus, not only did a resistance measurement show the importance and effect of conditioning but it also served to diagnose noisy or porous, anionic membranes.

### 3.3.2 Optimisation of membrane production conditions for electrode response.

Membranes were produced by the previously described procedures (Sections 2.3.2 and 2.3.3) and subsequently hydrolysed. The main success criteria used during this initial study was a linear (preferably Nernstian)  $\text{Ca}^{2+}$  calibration over a wide activity range. Various parameters, the majority interdependent,

TABLE 3-3. Effect of membrane composition on physical and electrochemical properties.

<u>Membrane</u>	<u>TAP % m/m</u>	<u>ABIN % m/m</u>	<u>THF solubility<sup>a</sup></u>	<u>Physical properties of cast membranes</u>	<u>Electrochemical Properties</u>
A	2.5	0	sol.	Elastic, clear	Short linear range, low slope
B	5	2.5	insol.	Elastic, clear, sl. yellow	Functional membrane Nernstian response.
C	2.5	5	insol.	Elastic, opaque	No response. High resistance
D	5	10	insol.	Clear with opaque inclusions	No response.
E	5	15	insol.	Bubbled, opaque inclusions	No response
F	15	2.5	insol.	Elastic, clear, yellow	V. short linear range, low slope.
G	50	5	insol.	Oily, yellow, rigid	Poor response. Low slope.
H	100	5	insol.	Thick, rigid with oily surface	Poor response

a - before hydrolysis

b - after hydrolysis for 5 hours in 1% aqueous NaOH solution under reflux.

were analysed and those of importance determined. The main variables affecting response were the amount of monomer and initiator and the degree of hydrolysis.

### 3.3.2.1 Solution cast membranes.

The effect of making large changes in solution-cast membranes may be seen in Table 3-3, where the TAP levels were increased from 2.5 to 100% m/m and ABIN levels from 0 to 15% m/m. The solubility in THF of the membrane before hydrolysis was used as an indicator of cross-linking and the response after hydrolysis was the response to  $\text{Ca}^{2+}$  ions. Membrane A indicated that low levels of monomer led to a THF-soluble membrane. This indicated a low level of cross-linking which resulted in a low slope ( $5\text{-}10\text{mV.pCa}^{-1}$ ) over a narrow range (pCa 4-2). The use of 5% m/m TAP and 2.5% ABIN resulted in the production of insoluble and electrochemically-functional membranes. Increasing the levels of ABIN with low levels of TAP (membranes C, D and E) resulted in membranes which were cross-linked yet which had poor physical properties, gave no response to calcium ions and were of very high resistance ( $>10^{10}\Omega$ ). This, seemingly contradictory, observation was due to cross-linking which was not entirely due to the phosphate monomer. Instead, the butadiene chains were being homo-cross-linked by the action of the greater initiator (ABIN) quantity, resulting in membranes showing no usable calcium response and having a high resistance. As the level of TAP monomer was increased (membranes F and G) until poly (TAP) was being produced (membrane H) the membranes became increasingly rigid. Despite showing some calcium response

TABLE 3-4 Effect of hydrolysis conditions on the physical and electrochemical properties of polymeric ion-exchange electrodes

<u>Membrane</u>	<u>TAP</u> <u>% m/m</u>	<u>ABIN</u> <u>% m/m</u>	<u>Hydrolysis<sup>a</sup></u>	<u>Solubility</u> <u>in THF<sup>b</sup></u>	<u>Slope<sup>c</sup></u> <u>mV.pCa<sup>-1</sup></u>	<u>Appearance</u>
1	5.0	2.5	5 h 1% aq. NaOH	sol.	+16	Milky, opaque
2	4.5	2.5	3 h 1% aq. NaOH	sol. (12h)	+24.2	Clear, becoming yellow-brown on hydrolysis
3	4.86	2.6	1 h 1% aq. NaOH	Sl.sol.	+29.5	Mainly clear, yellow on hydrolysis
4	4.54	2.5	20 h H <sub>2</sub> O	Sl.sol.	+29	Dark brown and brittle
5	4.4	2.5	5 h 5% KOH/MeOH	Insol.	+30	Clear, pale yellow, tough and elastic

a - Conditions refer to reflux

b - After hydrolysis

c - Conditioned in 0.1M CaCl<sub>2</sub> solution.

the properties of these membranes were not favourable. On the basis of these initial results the use of 5% m/m TAP and 2.5% m/m ABIN was further investigated.

Table 3-4 shows the effect of hydrolysis conditions on the response of electrodes produced from membranes containing the optimised levels of reactants. Originally, 5% aqueous NaOH hydrolysis was used, membranes being refluxed in this medium for 5 hours. This treatment resulted in a membrane which, before hydrolysis was insoluble in THF, but after hydrolysis became soluble. This was due to the polymer matrix being subjected to cleavage such that the cross-links which were produced during the polymerisation stage were being broken during the rather severe hydrolysis step. With membrane 2, the hydrolysis time was reduced to 3 hours. The effect of this decrease in the degree of hydrolysis was to decrease the solubility of the hydrolysed membrane and to increase the calibration slope. A further reduction to a 1 hour hydrolysis time (membrane 3) resulted in a membrane which was only slightly THF-soluble and which exhibited a Nernstian slope. This series of three membranes indicated that by decreasing the hydrolytic degradation, the physical and electrochemical properties were greatly improved. Membrane 4 showed the deleterious effect of boiling a membrane in water for an extended period. Although retaining much of the cross-linking and concomitant properties the membrane became brittle and brown due to the thermal degradation occurring at 100°C with what was a destabilised polymer.

The use of aqueous hydrolysis was shown to be capable of producing the ion-exchange sites necessary for a functional electrode. However, the use of this resulted in the chemical degradation of the structure which had been produced during polymerisation. Thus, the rather severe aqueous hydrolysis was changed in favour of methanolic hydrolysis. This solvent was more compatible with a polymeric matrix, had a lower boiling point than water yet was capable of dissolving an alkali metal hydroxide. Use of 5% methanolic KOH under reflux for 5 hours resulted in an insoluble membrane (Membrane 5) with favourable electrochemical properties.

This first study had shown that there were two opposing effects occurring during production of electrode membranes. In the first process, the organophosphate monomer was being used to form a covalently-bound sensor which also served to cross-link the polymer matrix. In the second process, hydrolysis of this polymer gave a dialkylphosphate ion exchange site, but hydrolysis also tended to degrade the polymer.

This effect is further demonstrated by the results in Table 3-5. A series of membranes was produced in which the amount of cross-linking and the degree of hydrolysis were varied. This was brought about by a reduction in both monomer and initiator concentration and by varying the strength of the hydrolysis medium.

TABLE 3-5 Effect of membrane composition and hydrolysis conditions on physical and electrochemical properties.

Membrane	TAP % m/m	ABIN % m/m	Hydrolysis <sup>a</sup>	Solubility in THFb	Slope <sup>c</sup> / mV.pCa <sup>-1</sup>	Appearance
5a	4.4	2.5	5 h 5% KOH/MeOH	Insol.	+30	Clear, pale yellow tough and elastic
5b	4.4	2.5	5 h 10% KOH/MeOH	Sol.	+35 decreasing to +17 after 20d	Clear, yellow-brown
6a	2.2	1.26	5 h 5% KOH/MeOH	Insol.	+24 decreasing to +15 after 3d	Clear, pale yellow
6b	2.2	1.26	5 h 10% KOH/MeOH	Sol.	-19	Brown, becoming brittle
7a	1.0	0.55	5 h 5% KOH/MeOH	Sol.	+25	Clear and colourless
7b	1.0	0.55	5 h 10% KOH/MeOH	Sol.	-12	Brown
8	0	0	5 h 5% KOH/MeOH	Sol.	-17	Clear and Colourless Pure SBS membrane

a - Conditions refer to reflux

b - After hydrolysis

c - Conditioned in 0.1 M CaCl<sub>2</sub> solution.

Membrane 5 was hydrolysed for 5 hours in 5% (membrane 5a) or 10% (membrane 5b) methanolic KOH. Membrane 5a retained some elasticity, was insoluble in THF and showed a Nernstian calibration slope. Membrane 5b was slightly soluble in THF and showed a deterioration in both electrochemical and physical properties. This was consistent with degradation by the stronger hydrolysis conditions. Decreasing the amounts of TAP and ABIN by 50% might have been expected to result in a halving of the amount of cross-linking in the membrane. This was assuming that all cross-linking had been brought about by the allylic monomer, TAP. Membrane 6 contained only half the amounts of TAP and ABIN used in membrane 5 and indeed, the amount of cross-linking was seen to be decreased. Although 6a resulted in a membrane which was insoluble, the calibration slope was sub-Nernstian and rapidly deteriorated. An increase in the degree of hydrolysis effected by increasing the strength of the methanolic KOH to 10% resulted in a brown THF-soluble membrane (6b) whose calibration slope was negative i.e. anionic.

The reason for the observed negative slope is thought to have arisen for two reasons. Firstly, the ion-exchange site density was decreased, but, more importantly, the membrane itself was rendered microporous by the combined effects of reduced monomer/initiator concentration and increased strength of hydrolysis. A microporous membrane might be expected to exhibit an anionic response due to the passage of chloride

ions through the membrane. This is a similar effect to that seen with some paraffin and 'crack-type' of electrodes discussed in Chapter 1.

A further halving of cross-linking was made in membrane 7 which was subsequently THF-soluble. When hydrolysed in 5% methanolic KOH, (7a) the calibration slope was sub-Nernstian and decreased rapidly over a 3 day period. Use of an increased degree of hydrolysis (10% methanolic KOH) resulted in a brown, anion-responsive membrane, (7b).

A membrane made from pure SBS (with no cross-linking) and hydrolysed in 5% methanolic KOH gave what was, in effect, an 'empty' membrane (membrane 8). The membrane was processed and treated in an identical manner to the others. As might have been expected, the membrane was soluble in THF and exhibited an anionic response.

These results demonstrated the effect of decreasing the amount of cross-linking from the optimum (5% TAP, 2.5% ABIN, 5% methanolic KOH/5 hrs.). They also served to indicate the interdependence of cross-linking and hydrolysis conditions and the importance of choosing compromise conditions such that cross-linking was not being generated in one step and then being destroyed in the next. Decreasing the level of cross-linking eventually resulted in the production of THF-soluble membranes which gave rise to electrodes responding to the anion ( $\text{Cl}^-$ ) rather than the cation ( $\text{Ca}^{2+}$ ).

### 3.3.2.2 Lyophilised/hot-pressed membranes.

The only controllable variables during the lyophilysis step were the solvent, the solvent volume and the rate of evaporation. THF had proved to be the best solvent for solution casting, so it was again used and a 10% w/v solution of SBS in THF was used. The rate of evaporation was dependent upon the pump used - the same pump and solvent vapour traps were, therefore, used throughout.

Pressing conditions for SBS were first optimised and found to be 140°C, 10 tons ram force and 5-10 minutes reaction time (see Section 2.4.2.1). A reaction time of 10 minutes was used initially and a membrane prepared which contained the same constituents that had been optimised for a solution-cast membrane. The resulting membrane was extremely tough but showed a large amount of bubbling. This was at first thought to be the result of a poor polymer batch, but a repeat using freshly-prepared reagents yielded the same result. The reason for this bubbling was thought to lie in the decomposition of ABIN;



during which free radicals are formed and nitrogen is evolved. For instance, if 0.25g ABIN were used, then its complete decomposition would yield 34cm<sup>3</sup> N<sub>2</sub> gas (at STP). In the confines of the press, this would be expected to give rise to

bubbling within the liquid polymer film. Thus, the use of ABIN was discontinued.

Benzoyl peroxide, another commonly used initiator, was also avoided for this reason as under certain conditions  $\text{CO}_2$  may be evolved with a similar effect. A high-temperature initiator well-suited to the press conditions and the polymer system was used - dicumyl peroxide (DCP). Incorporation of 5% TAP and 2.5% DCP into SBS resulted in production of a very tough, clear and insoluble polymer film. No amount of hydrolysis produced a calcium response with this membrane although the use of 25% aqueous NaOH eventually resulted in partial dissolution of the polymer matrix. These observations were consistent with a very high amount of cross-linking and this was corroborated by the very high resistance ( $>10^{10}\Omega$ ) of electrodes using such a membrane.

Experiments were continued in an effort to reduce the level of cross-linking. A decrease in the press temperature was not feasible as the polymer would not have flowed, so a decrease in reaction time to 5 minutes was implemented and the initiator level was reduced to 0.1%. Even under these conditions, well-crosslinked but non-functional membranes resulted when using 5% TAP. A series of membranes was then prepared in which no initiator whatsoever was used as it was suspected that sufficient free radicals would be produced by thermolytic fission. Additionally, levels of TAP were significantly reduced. A series of six membranes is shown in Table 3-6 along with their respective electrode responses.

TABLE 3-6

Electrochemical Properties of membranes produced by lyophilysis/hot-pressing.

MEMBRANE	TAP CONTENT (% w/w)	HYDROLYSIS <sup>*</sup>	RESPONSE
1	0	5 hrs. 5%	Anionic. -22 mV/pCa.
2	4.5	24 hrs. 5%	No response, v.high.res.
3	0.129	10 hrs. 5%	+7 mV./pCa.
		5 hrs. 10%	+18.6 mV./pCa
4	0.496	24 hrs. 5%	Sl.response (+5 mV./pCa.)
5	0.973	10 hrs. 5%	" "
6	1.0	5 hrs. 5%	" "
		24 hrs. 5%	+18 mV./pCa.

\* Methanolic KOH under reflux.

Press conditions - no initiator

- 140°C

- 10 tons ram force

- 5 mins.

Membrane 1 was made solely of SBS but was found to be less soluble in THF than its solution-cast counterpart, taking some 10 hours to dissolve. This indicated that sufficient free radicals had been generated in the SBS to cause cross-linking reactions to occur in the butadiene chains. On hydrolysis for 5 hours in 5% methanolic KOH, however, an anionic response of comparable magnitude to that shown by a solution-cast pure SBS membrane was observed. Membrane 2 demonstrated the effect of using levels of TAP used in solution casting, but with no formal initiator. A very high level of cross-linking was produced and even after 24 hours hydrolysis there was no response and the membrane acted as an insulating film. The remainder of the series (membranes 3-6 inclusive) showed that even at very low TAP levels, strong hydrolysis was needed to coax any response from the membrane, indicating prohibitively high levels of cross-linking. Slopes of these electrodes never exceeded  $+20 \text{ mV.pCa}^{-1}$  and the generally high resistances tended to result in very noisy responses.

The electrochemical performance of electrodes made from lyophilised and hot-pressed membranes was very poor. Physically, the membranes were extremely tough and were very good as rubber films. However, as ion-exchange membranes, these membranes were very poor. The reasons for this are complex but probably lie, to some extent, in the different polymer morphology generated during hot pressing compared to that resulting from

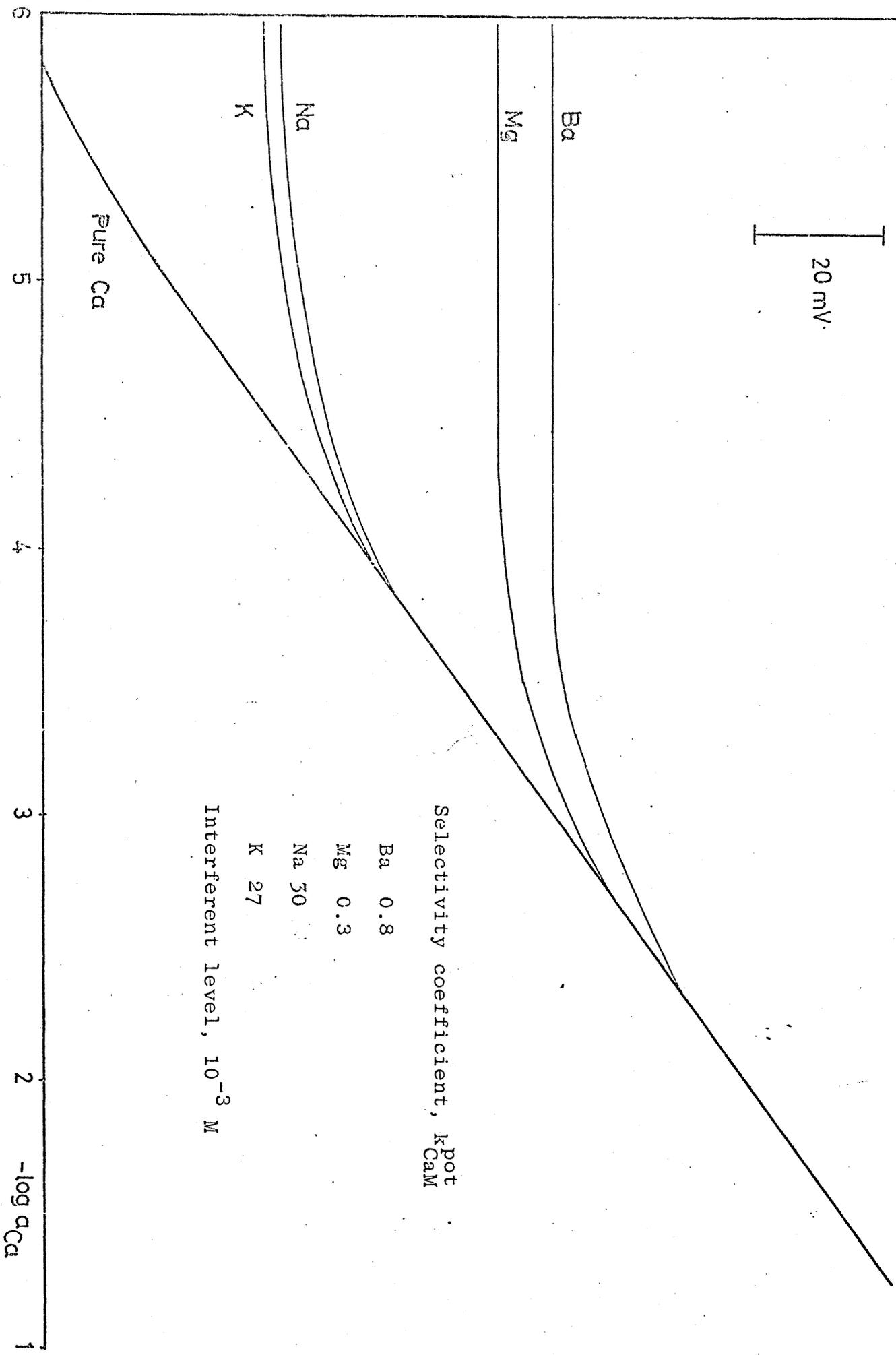
solution casting. Also, during the hot-pressing of such a destabilised/purified material, the reactions forming crosslinks were much more efficient than those operating during solvent casting. This led to comparatively high levels of cross-linking which resulted, in turn, in membranes which formed non-conducting films unsuitable for use in ISE. Thus, despite the advantages of controllability, reproducibility and convenience which might be expected of hot-pressing, the technique is inferior to solution casting when using SBS/TAP as only the latter technique produces functional ISE membranes.

### 3.3.3 Selectivity.

The selectivity of an ISE may be expressed as a selectivity coefficient or may be depicted by selectivity plots as described in Section 3.1.3. Mixed solution techniques (Section 3.1.3.1) and selectivity plots are used here to show the selectivity behaviour of the electrodes produced. This approach allows a rapid, realistic appraisal of the utility of an electrode for a particular application providing that the conditions of measurement are specified.

Selectivity plots have been constructed with activity coefficients ( $\gamma_{Ca^{2+}}$ ) being calculated for each point using the ION program (Appendix 1). This approach allowed the use of simple mixed solutions and enabled evaluation of selectivity for single Ca-M pairs without the complication of buffered systems.

Figure 3-3 Selectivity plots-Membrane 5a



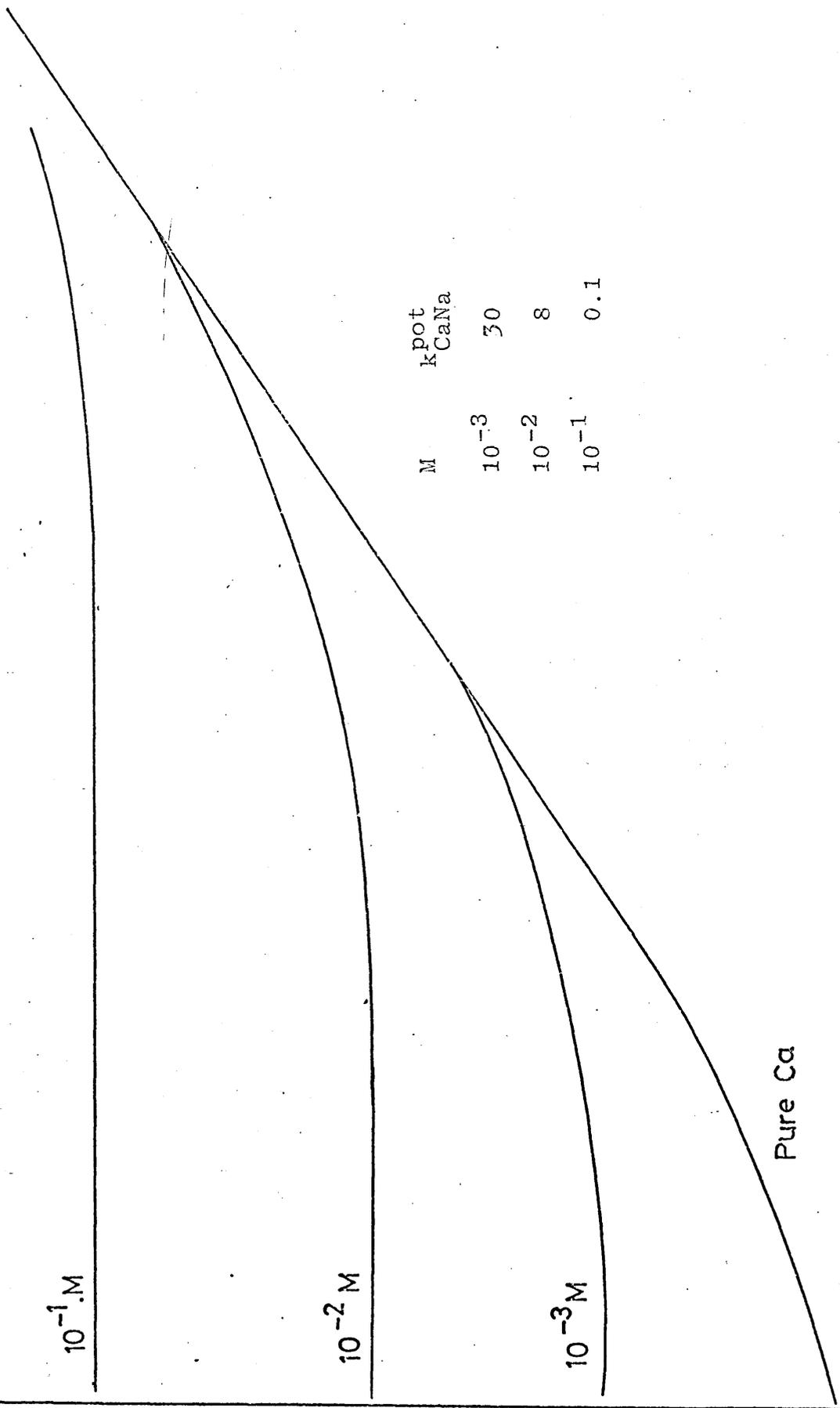
Electrodes were screened for interference from  $Mg^{2+}$ ,  $Ba^{2+}$ ,  $Na^+$  and  $K^+$ . The interference from a background level ( $10^{-3}M$ ) of these ions upon a 5% TAP membrane (5a) is shown (Figure 3-3). A definite trend of selectivity was immediately visible where the divalent and monovalent lines lay in two separate groups - the divalent ions showing the highest interference. Potentiometric selectivity coefficients,  $k_{CaM}^{pot}$  were calculated from the 9 mV. deviation (section 3.1.3.1). Values of  $k_{CaM}^{pot}$  for  $M=Ba$  and  $Mg$  were 0.8 and 0.3 respectively indicating a small but definite selectivity for calcium. The values,  $k_{CaM}^{pot}$  for  $M = Na, K$  were numerically much higher (30, 27 respectively) and further stress the point raised in Section 3.1 that care must be exercised when interpreting  $k^{pot}$  values. The high figures for  $Na$  and  $K$  are the result of the power term in equation 3-9/3-10 and the true effect of the interferent may be seen from the plots (Fig.3-3). In fact,  $10^{-3}M$  monovalent interferent exerted only one-tenth the effect of the same level of divalent interferent ion. This numerical anomaly may be seen more plainly in Figure 3-4 where the effect of increasing  $Na$  ion concentration on the response of membrane 5a is shown. At  $10^{-3}M Na^+$  background  $k_{CaNa}^{pot} = 30$ , but the electrode still showed an extended linear calcium calibration range ( $10^{-4}$  to  $10^{-1}M$ ). An increase in the level of  $Na^+$  to  $10^{-1}M$  resulted in the electrode response to

EFFECT OF SODIUM CONCENTRATION ON ELECTRODE RESPONSE

Figure 3-4 MEMBRANE 5a

20mV

mV



M	k <sub>CaNa</sub> <sup>pot</sup>
10 <sup>-3</sup>	30
10 <sup>-2</sup>	8
10 <sup>-1</sup>	0.1

5

4

3

2

1

-log aCa

6

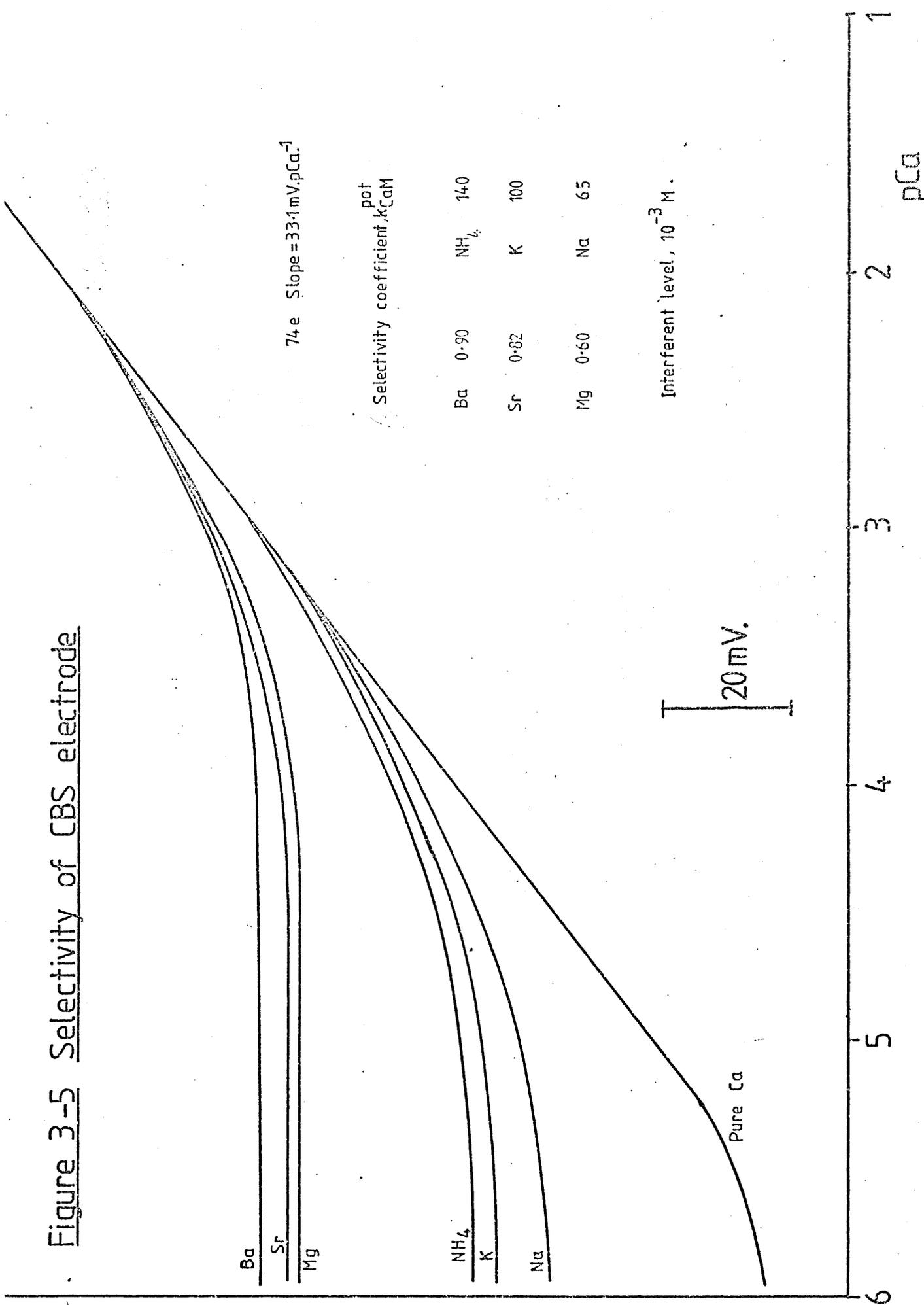
Pure Ca

10<sup>-1</sup> M

10<sup>-2</sup> M

10<sup>-3</sup> M

Figure 3-5 Selectivity of CBS electrode



pCa

1  
2  
3  
4  
5  
6

mV

Figure 3-6 Selectivity of CBS electrode.

20mV.

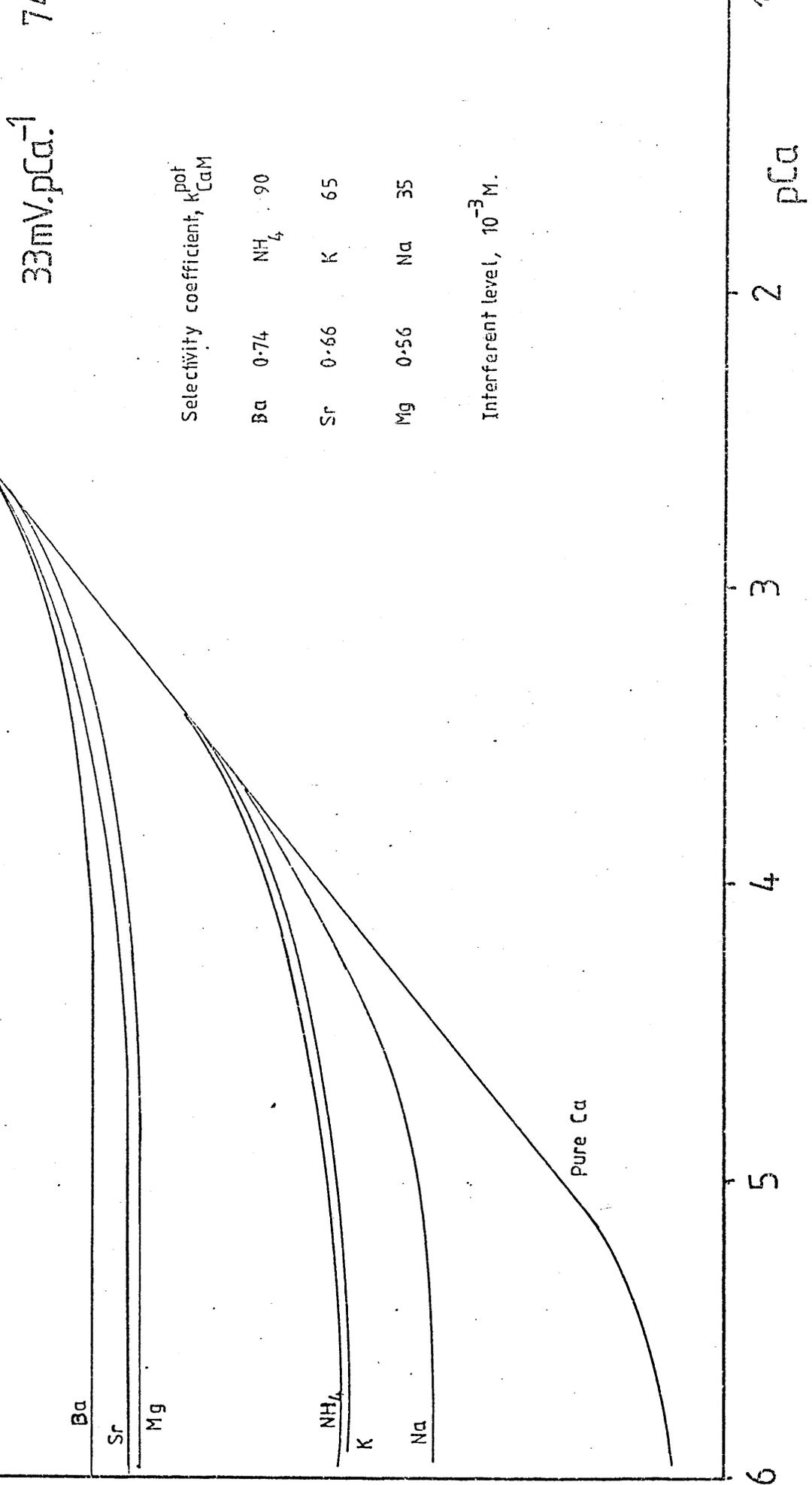
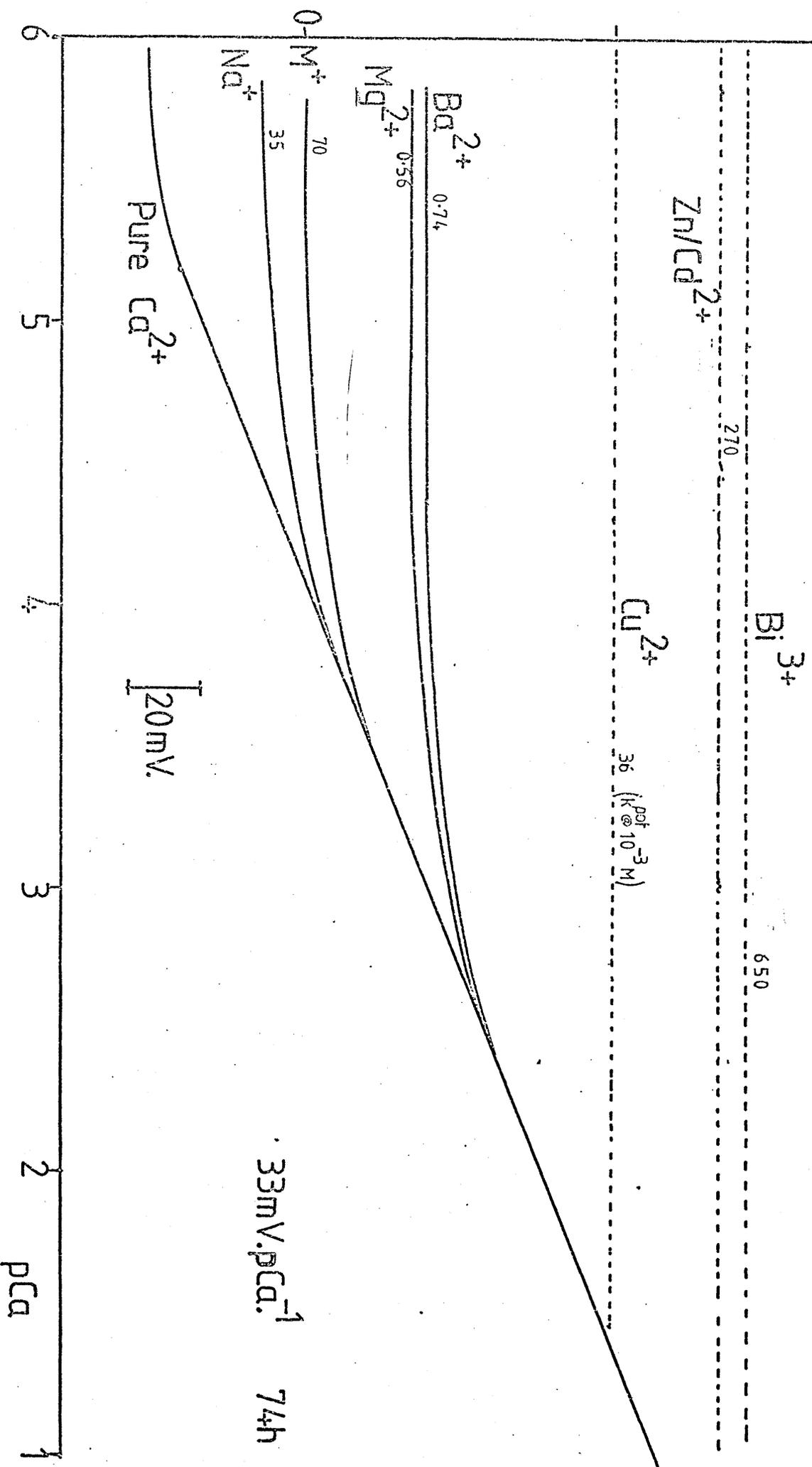


Figure 3-7 Overall selectivity of CBS electrode.

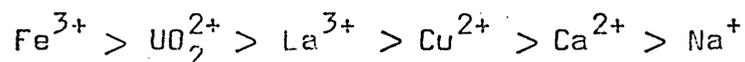


Ca<sup>2+</sup> being overwhelmed by the background level of Na<sup>+</sup>. However, the  $k_{CaNa}^{pot}$  values, which decrease with increasing interferent concentration suggest the electrode would function better in 10<sup>-1</sup>M Na than in 10<sup>-3</sup>M Na. That this is not the case may be plainly seen from the selectivity plots (Fig.3-4).

Selectivity plots for two other 5% TAP electrodes (Figs. 3-5 and 3-6) indicate numerical values of  $k_{CaM}^{pot}$  which are similar to those found for membrane 5a (Fig.3-3). In addition, values for interference by Sr<sup>2+</sup> and NH<sub>4</sub><sup>+</sup> further indicate a separation of selectivity by valence. A further extension of the selectivity study (Figure 3-7) indicated the overall pattern of interference and selectivity. In particular, the effect of transition metal and polyvalent cations may be seen. The interference pattern observed was;

$$M^{3+} > Cd^{2+} = Zn^{2+} > Cu^{2+} > Ca^{2+} > Ba^{2+} > Sr^{2+} > Mg^{2+} > M^{+}$$

which is in agreement with the absorption sequence found by Kennedy<sup>144</sup>;



for hydrolysed poly(TAP).

This observation of interference from polyvalent and transition metal cations is consistent with the interference by Zn<sup>2+</sup> generally seen with Ca ISE<sup>115,116</sup>. Interference from La<sup>3+</sup> has also been found to be severe<sup>140</sup> and the above series may be expected to hold for phosphate exchangers generally. However, the effect of solvent mediators on the extraction behaviour

Figure 3-8

Membrane 5a

pH response

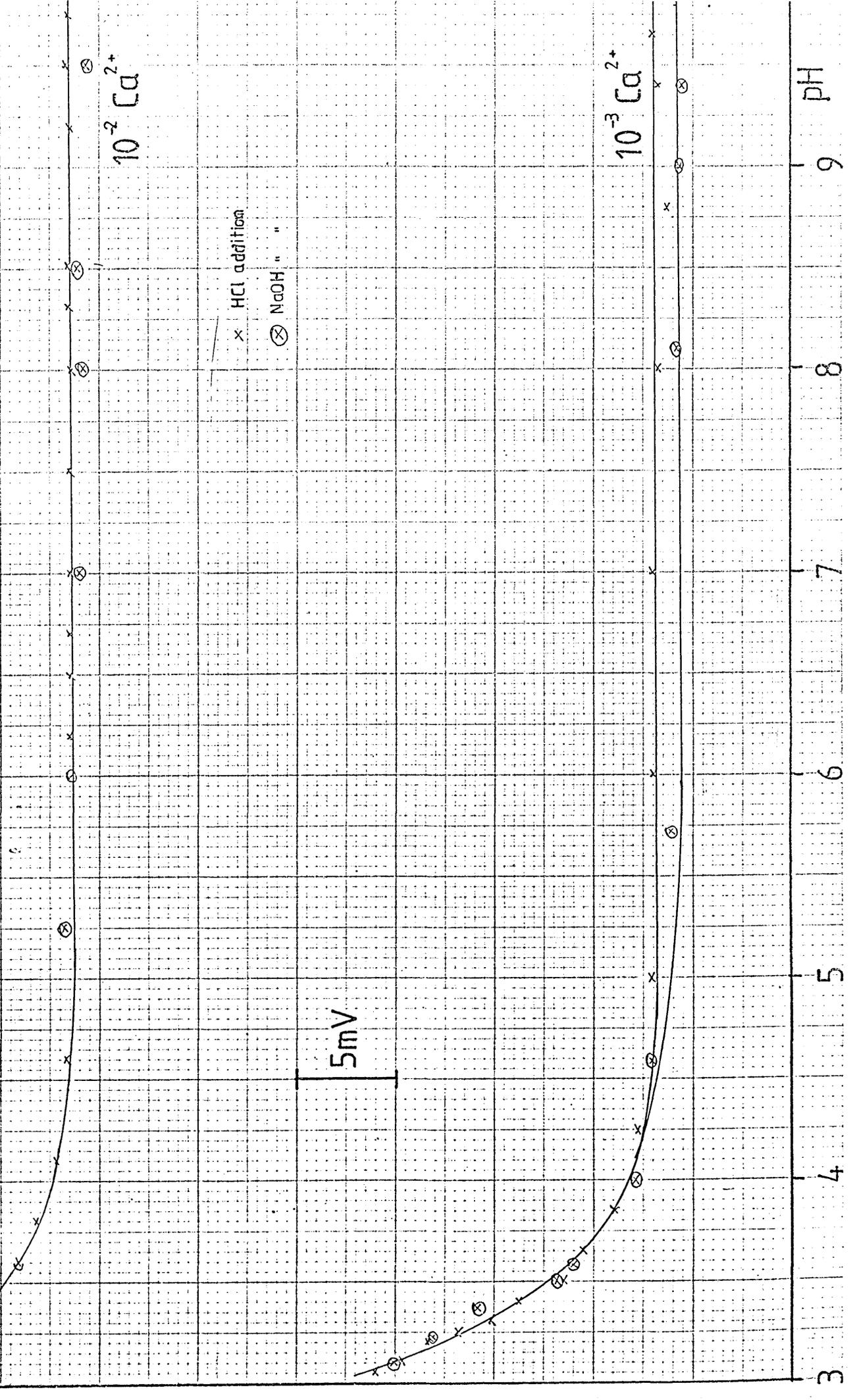


Figure 3-9 Effect of selected cations on electrode response

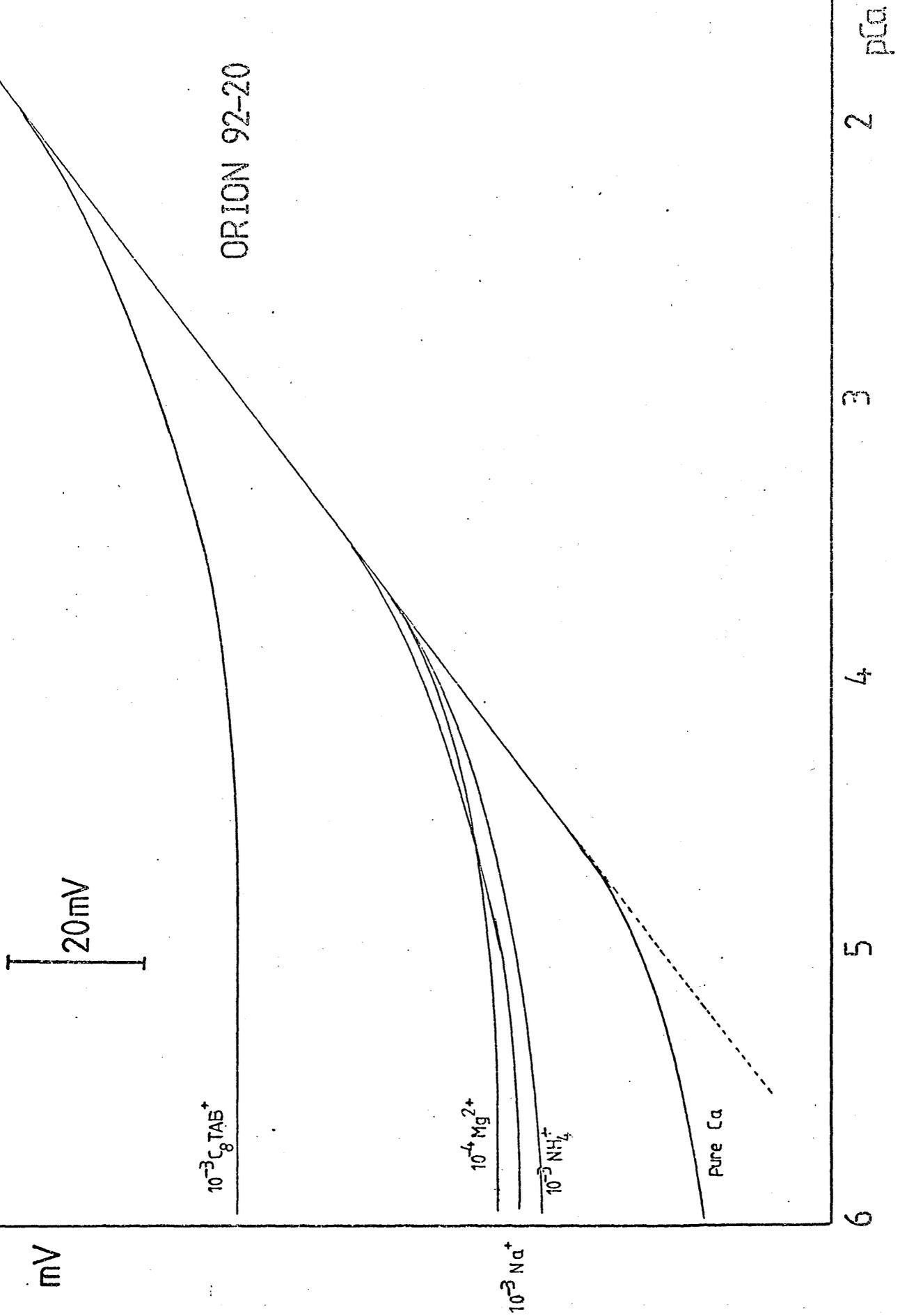
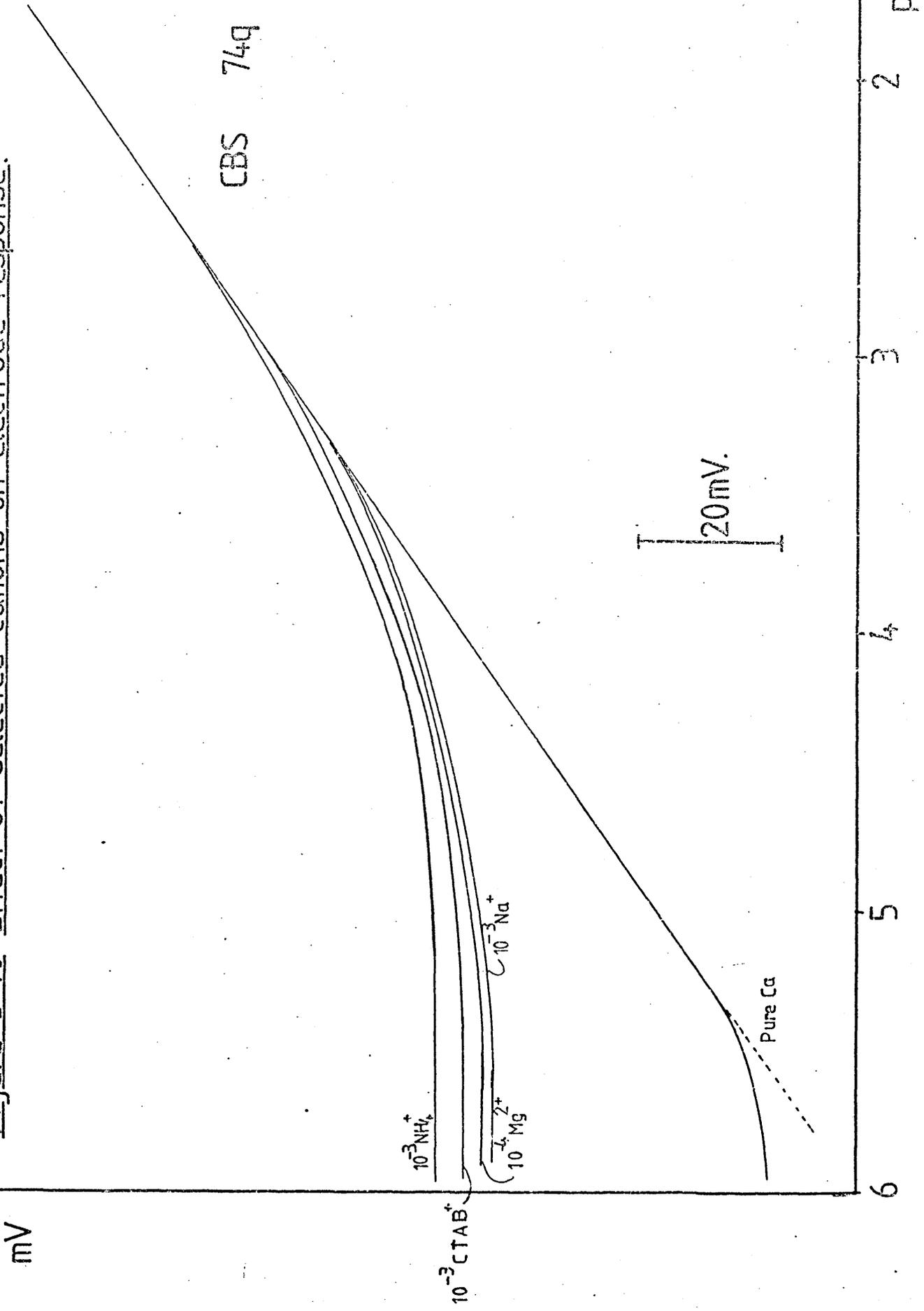


Figure 3-10 Effect of selected cations on electrode response.



ELECTRODE	INTERFERENT	CONCN. (M)	SELECTIVITY COEFF. NT, K <sup>POT</sup>	SLOPE (MV DECADE <sup>-1</sup> )
ORION	NH <sub>4</sub> <sup>+</sup>	10 <sup>-3</sup>	27	
	Mg <sup>2+</sup>	10 <sup>-3</sup>	0.032	28.5
PVC	NH <sub>4</sub> <sup>+</sup>	10 <sup>-3</sup>	17	
	Mg <sup>2+</sup>	10 <sup>-3</sup>	0.066	31.0
	NA <sup>+</sup>	10 <sup>-2</sup>	0.36	
SBS	NH <sub>4</sub> <sup>+</sup>	10 <sup>-3</sup>	76	
	Mg <sup>2+</sup>	10 <sup>-3</sup>	0.6	34.0
	NA <sup>+</sup>	10 <sup>-2</sup>	9.3	

Table 3-7 Selectivity comparison of three electrodes.

of this series may be sufficient to alter the position of some of the members within it.

Other important cations which might be expected to interfere with a calcium ISE response are  $H^+$  and surfactants. The pH response of membrane 5a has been determined at two different calcium ion activities (Fig.3-8) and indicated a very wide pH working range (pH 4,4.5 to 10). The graph shows none of the 'dips' characteristic of other calcium ISE (e.g. Orion 92-20/ Fig.1) at low pH values. A comparison of the selectivity of an Orion 92-20 (Fig.3-9) and a TAP covalently-bound sensor (CBS) electrode (Fig.3-10) was made for selected cations. In particular, selectivity for  $Ca^{2+}$  over a surfactant (Octyltrimethyl-ammonium bromide,  $C_8TAB$ ) and ammonium ions was assessed. The Orion ISE showed significant interference from  $C_8TAB$  ( $k^{pot} = 1.5 \times 10^3$ ) whereas with the CBS electrode (74q, Fig.3-10) only the interference typical of a monovalent cation was observed. The interference of  $NH_4^+$  ions on both types of electrode was also found to be high. The Orion electrode and a PVC matrix electrode made from the same exchanger were both found to give poor  $Ca^{2+}$  over  $NH_4^+$  selectivity whereas the CBS electrode merely registered  $NH_4^+$  as a monovalent cationic interferent (Table 3-7).

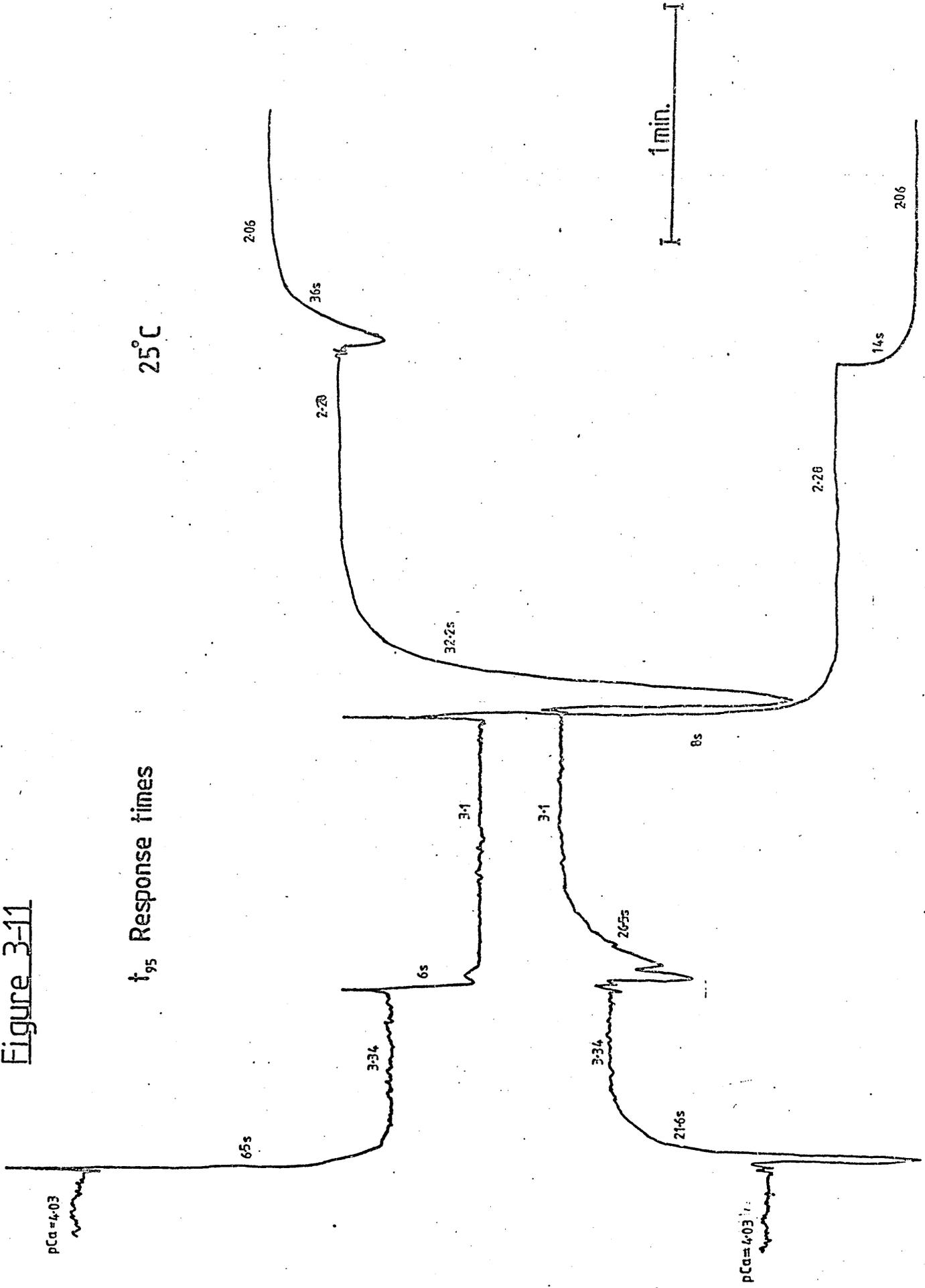
#### 3.3.4 Response Time.

Dynamic, as opposed to static, response times have been determined. It was felt that not only was the dynamic response more consistent with analytical needs but it also supplied some

Figure 3-11

$t_{95}$  Response times

25°C



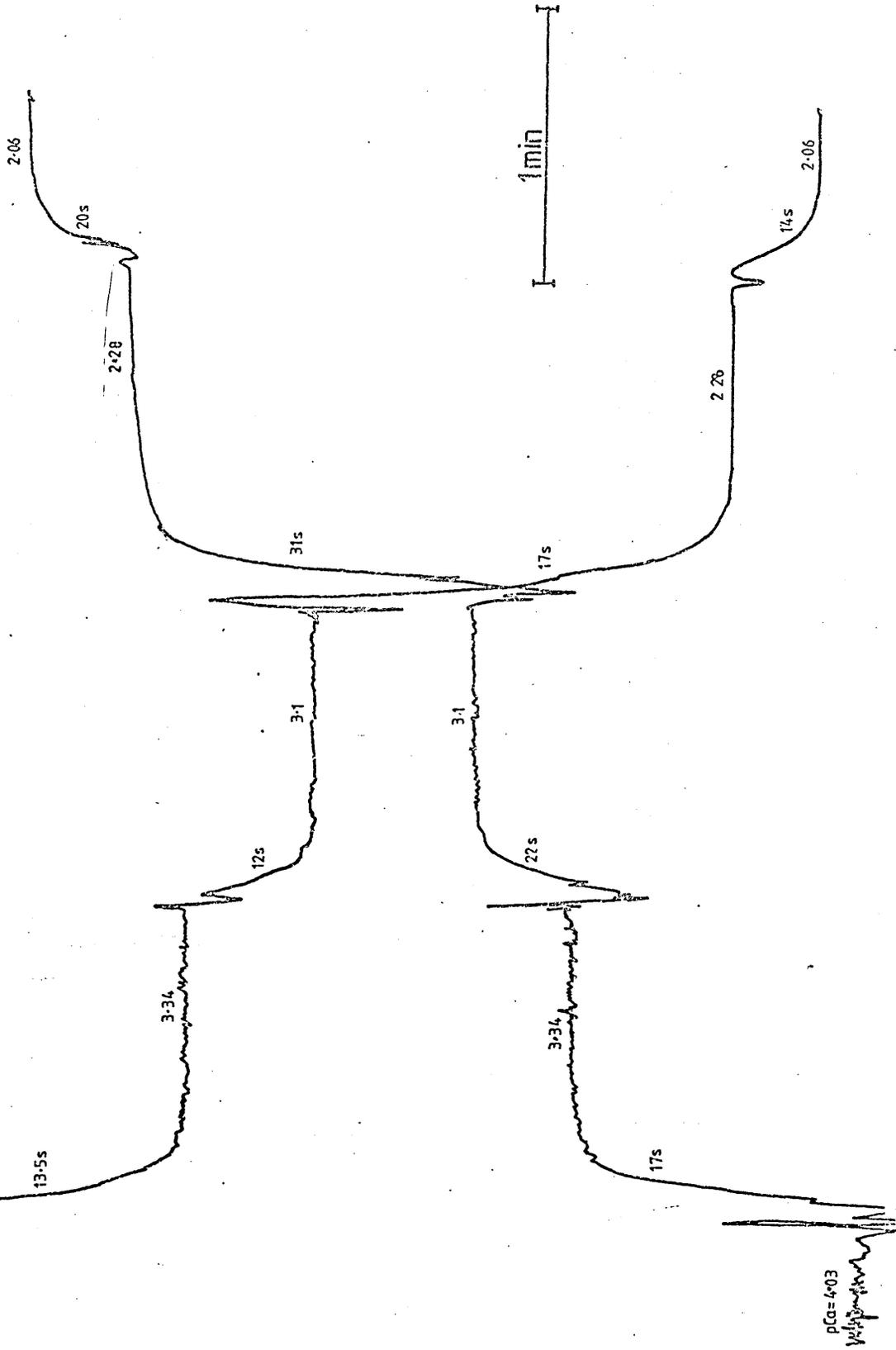
749

pCa = 4.03

Figure 3-12

$t_{95}$  response time

25°C



pCa = 4.03

92-20

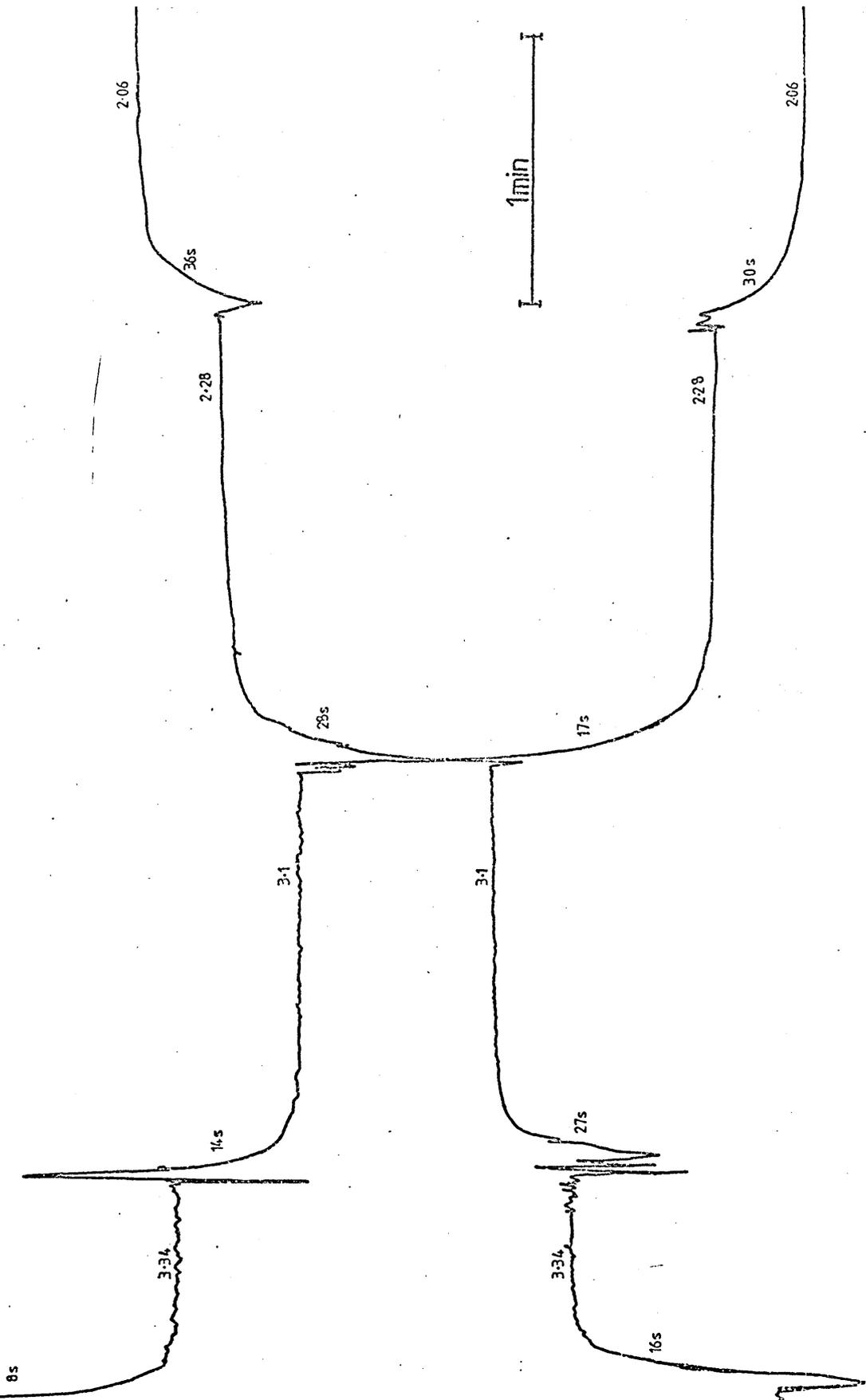
74q

pCa=4.03

Figure 3-13.

$t_{95}$  response time

25°C



pCa=4.03

92-20

*[Handwritten signature]*

mechanistic data. The measurement of ultimate dynamic response times of a fast ISE ( $<5s$ ) is fraught with some difficulty. In particular, the solution determinand activity must be changed very rapidly and the instrumental dead time needs to be very short (milliseconds). Requirements for instrumentation and the apparatus for effecting rapid known concentration changes were, therefore, high. Attempts to measure response times of less than 5s met with limited success as turbulence in rapidly-stirred solutions tended to cause electrostatic noise and large stirring potentials. In addition, entrainment of air bubbles under the recessed Orion body tip occurred in such turbulent solutions. A comparative approach was therefore adopted in which standardised conditions were adopted. Electrodes were run in parallel, i.e. in the same solution and with respect to the same reference electrode, and stirring was at a constant 250 r.p.m.

The results obtained using this approach (Figs. 3-11, 12 and 13) showed that the CBS electrode (74q) was consistently faster than the Orion 92-20 calcium ISE. Over a series of such measurements at  $25^{\circ}C$ , the mean of the  $t_{95}$  response time at all determinand levels was found to be less for the CBS than for the Orion electrode (Table 3-8). The consistency of the CBS electrode times was considerably better than that for the Orion electrode, in some instances, the variation in

TABLE 3-8  $t_{95}$  Response time comparison.

pCa=4.03 → 3.34 → 3.1 → 2.28 → 2.06

Electrode				
92-20	21.6	26.5	32-2	36
CBS	6.5	6	8	14
92-20	15	22	18	22
CBS	12	14	13.5	10
92-20	11	17	16	22.5
CBS	9.5	7.2	11	18
92-20	36	47	48	63
CBS	10	11.5	6.2	14.5
92-20	16	27.5	28	36
CBS	18	14	17	30
92-20	14	16	24	21.5
CBS	11	10	14	28.5
92-20	17	22	31	20
CBS	13.5	12	17	14
<u>92-20</u> Mean	18.7	25.4	28.2	31.6
S.D.	8.3	10.4	10.7	15.5
<u>CBS</u> Mean	11.5	10.7	12.4	18.4
S.D.	3.6	3.1	4.2	7.8

All results are for  $t_{95}$  values in seconds.

$t_{95}$  for the latter was 50% from run to run. Response times of the 92-20 were slightly affected by the presence of  $Mg^{2+}$  ions whilst a CBS electrode showed no effect and a PVC electrode seemed significantly slowed down. However, the electrostatic nature of the PVC matrix electrodes fabricated precluded their use in a stirred system and further investigation of this effect was not pursued.

### 3.3.5 Lifetime of electrode membranes.

It is difficult to assess the lifetime of an ion-selective electrode. Ideally, a dedicated flow-through system and a continuous 'real-life' stream would be used and the lifetime of electrodes could be assessed under identical conditions. As no such apparatus was available, the useful lifetime was found from experience with usage. Early electrodes which had been subjected to severe hydrolysis conditions displayed lifetimes which were limited to 3 to 30 days by the decrease in the calibration slope. This decrease in slope may be used as a criterion of useful lifetime.

In the case of membrane 5a, the slope did not begin to degenerate until after 9 months of use when it became less than  $26 \text{ mV.pCa}^{-1}$ . A section of the same membrane was hydrolysed after a period of 13 months and was found to result in a perfectly functional electrode with a lifetime in excess of 3 months. The performance of this second electrode was equally

as good as that observed for electrodes from the first batch.

In fact the lifetime of the CBS electrode was not governed by loss of the sensor into the test solution as for other Ca ISE. In the CBS the sensor cannot be leached out and can only be poisoned or 'used up'. The two latter cases did not seem to occur, the lifetime being limited by the properties of the SBS polymer used. The purified (destabilised) polymer naturally crosslinked across the remaining unreacted butadiene chain segments under the influence of ambient U.V. levels. This resulted in the development of brittleness and was found to give electrodes with high resistances (noisy responses) or 'crack' electrodes which were microporous to anions and, therefore, chloride-responsive. This appearance of cracks was not simply spontaneously caused by mishandling, but occurred naturally as the membrane crosslinked and became brittle and over-stressed. Thus, the limitation of lifetime is not dependent upon the sensor or its loss, but by the polymer to which the sensor group is covalently bound. It is, therefore, a technological problem and by the judicious choice and use of stabilisers the lifetime may be extended even further.

### 3.3.6 General analytical behaviour.

The general analytical utility of CBS electrodes will be shown in Chapter 5, but some indication will be given here. The limit of detection (lod) is, unlike other Ca ISE, not set by the finite solubility of the Ca-sensor complex. The sensor

TABLE 3-9. Data used to plot Figure 3-6 for selectivity of CBS electrode (74g)

[Ca <sup>2+</sup> ]	Pure Ca <sup>2+</sup>	Pure Ca <sup>2+</sup>	10 <sup>-3</sup> M Na <sup>+</sup>	10 <sup>-3</sup> M K <sup>+</sup>	10 <sup>-3</sup> M NH <sub>4</sub> <sup>+</sup>	Pure Ca <sup>2+</sup>	10 <sup>-3</sup> M Mg <sup>2+</sup>	10 <sup>-3</sup> M Ba <sup>2+</sup>	10 <sup>-3</sup> M Sr <sup>2+</sup>	Pur
10 <sup>-6</sup> M	-44.1	-42.8	-10.8	+0.1	+1.6	-44.0	+28.6	+34.5	+29.5	
10 <sup>-5</sup>	-29.0	-26.8	-8.9	+2.0	+3.4	-28.5	+29.0	+35.3	+31.2	-26
4x10 <sup>-5</sup>	-11.2	-8.1	-1.6	+5.6	+7.3	-10.3	+29.8	-	-	-9.
7x10 <sup>-5</sup>	-2.6	-1.9	+3.4	+10.8	+11.2	-2.1	+30.2	-	-	-1.
10 <sup>-4</sup>	+3.1	+4.5	-7.6	+12.0	+13.0	+2.5	+30.7	+36.6	+33.5	+3.
4x10 <sup>-4</sup>	+20.8	+21.5	+21.2	+23.4	+23.6	+19.4	+34.1	+27.9	+35.6	+21
7x10 <sup>-4</sup>	+28.3	+29.0	+28.1	+29.9	+29.6	+27.7	+36.8	-	+38.6	+28
10 <sup>-3</sup>	+34.5	+34.5	+34.0	+34.7	+33.8	+33.5	+39.1	+44.8	+41.0	+32
4x10 <sup>-3</sup>	-	-	-	+49.1	+47.9	+50.7	+50.0	+51.5	+50.8	+48
7x10 <sup>-3</sup>	-	-	-	+56.9	+55.7	+57.1	+58.0	+57.8	+58.2	+55
10 <sup>-2</sup>	+59.3	+61.0	+58.7	+62.4	+61.4	+62.0	+61.8	+61.8	+61.8	+60
2x10 <sup>-2</sup>	+68.2	+68.7	+68.0	+69.6	+69.3	+70.1	+68.5	+71.1	+67.8	+69
10 <sup>-1</sup>	+86.0	+89.4	-	-	-	+86.9	-	-	-	+87

Readings in mV at 25°C

cannot be lost from the membrane, so the lod would be set by the stability of the Ca-membrane complex. In practice, lod values of  $10^{-6}$  M  $\text{Ca}^{2+}$  are routinely observed and these appear only to be limited by problems of glassware contamination/adsorption or by the purity of reagents used and by the reality of diluting to these very low levels.

Run to run calibration precision is demonstrated by the results used to construct Figure 3-6 (Table 3-9). These figures are an average batch for a run involving fairly severe electrode treatment and show a precision better than  $\pm 1$  mV throughout the calibration range.

In terms of drift, the CBS electrodes performed extremely well. Typical day to day drifts found were;

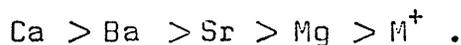
74h	Date	22/2	23/2	24/2	
	mV*	+36.5	+32.8	+34.5	
74q	Date	8/7	14/7	17/7	19/7
	mV*	+63.0	+67.1	+62.5	+60.6
74r	Date	28/6	3/7	8/7	
	mV*	+37.0	+37.0	+33.2	

\* reading for  $10^{-3}$  M  $\text{Ca}^{2+}$  solution @  $25^{\circ}\text{C}$ .

The above figures are for separate calibration points. Ideally, the same solution should be used and a continuous measurement made. This demands rather more sophisticated instrumentation and also the effects of 'bleed' of electrolyte through the reference electrode junction may disturb the reading (especially for poorly-selective electrodes).

### 3.4 Conclusions.

The general analytical performance of a calcium selective electrode containing covalently-bound dialkylphosphate sensor groups has been evaluated. The best method of production of such ion exchange membranes was to cast from THF solution and to hydrolyse in methanolic KOH solution. Electrodes produced by these techniques exhibited Nernstian slopes over a very wide calcium activity range (pCa 6-1), a fast response time and a wide pH working range (pH 4 to 10). The selectivity of these electrodes was found to be in the order:



but selectivity was not generally as good as for many 'state of the art' Ca ISE. However, selectivity in the presence of  $\text{NH}_4^+$  and surfactant cations was as good and better, respectively. General analytical performance was better than most other Ca ISE, but attempts to improve selectivity would be necessary to allow wider exploitation and application. To this end modification of the phosphate ion exchange site was considered in an attempt to influence electrode selectivity. The approach to this modification and the subsequent effects are reported in the next chapter.

CHAPTER 4.

Production and Evaluation of membranes  
containing covalently-bound sensor  
groups other than TAP.

#### 4.1 Objectives

From the results presented in the previous chapter it is evident that functional membranes for Ca ISE may be produced containing a dialkylphosphate ion-exchange group covalently-bound to the C=C unsaturation of a synthetic polymer. The performance of these covalently-bound sensor (CBS) electrodes has been found to be advantageous, particularly in terms of their lifetime, response range and speed of response. In fact, when comparing the analytical performance of such an electrode to that of a PVC or phosphorylated membrane electrode<sup>138</sup> (Table 4-1), the advantages of a completely covalently-bound sensor are clearly seen. Despite the overall advantage to be gained from using a CBS electrode, such an electrode does have some shortcomings. In particular, the selectivity (e.g. to divalent cations) of a CBS electrode is inferior to that shown by other calcium ISE. However, the selectivity difference seen with monovalent interferents is less marked. In fact the response of a CBS electrode is less affected by surfactant cations than is that of a PVC or liquid membrane Ca ISE. However, the response of CBS electrodes is significantly affected by transition metal or multivalent cations. So, an improvement in electrode selectivity was sought, to add further to the advantages of a covalently-bound sensor electrodes.

TABLE 4-1 Comparison of electrode performance.

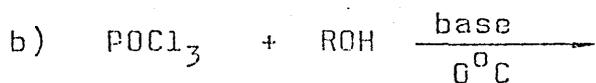
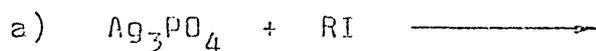
Characteristic	PVI matrix membrane <sup>a</sup>	Phosphorylated membrane <sup>a</sup>	This study
Detection limit /M	10 <sup>-5</sup>	1.2 x 10 <sup>-5</sup>	10 <sup>-6</sup>
Slope at 25°C/mV.pCa <sup>-1</sup>	30	29	30
pH range	5 - 9	5.5 - 8	4 - 10
Response time dynamic/s	2	1	1
Drift /mV. day <sup>-1</sup>	5	5	2
Operational lifetime/week	2	2	24
Selectivity coefficients			
K <sup>pot</sup> CaM	0.086	0.042	0.3
Na(10 <sup>-2</sup> M)	1.1	1.0	8

a. Reference 138.

In order to modify the selectivity of a CBS electrode, one might modify either the sensor group or the polymer matrix. It has already been shown, for PVC membrane electrodes, that improvements in selectivity could be induced by changing the sensor. Conversely, the use of matrix materials other than PVC had been to little advantage. In this study, SBS had been shown to act as a good model polymer matrix into which organophosphate ion-exchange groups could be incorporated. Thus, SBS was retained as the polymer matrix as it had been extensively investigated and, although SBS had shortcomings, these were known. It was, therefore, thought useful to modify the sensor group which could be accomplished by altering the monomer used. There was some restriction on the choice of monomer as it should meet the following requirements:

- a) the monomer should contain a  $\text{P}=\text{O}$  moiety or be easily convertible to such;
- b) it should also have residual C=C unsaturation to enable the combination of monomer and polymer (SBS).

Monomers of a form analogous to the already-used TAP were therefore required. Few such monomers are documented, and even fewer are commercially available despite the fact that this type of compound has been known for some considerable time.<sup>164</sup> However, various methods for the preparation of such materials were available<sup>165,166,167,168</sup> e.g:



c) Oxidation of trialkyl/allyl phosphite with  
air/ $\text{H}_2\text{O}_2$ .

Method b was the one of choice as the reactants were easily obtainable and purified. So, the identity of the alcohol would ultimately determine the characteristics of the phosphate exchanger. As was the case with unsaturated phosphates, few unsaturated alcohols were available. In particular, alcohols with both terminal C=C and -OH functionality were scarce.

Notwithstanding this, it might be advantageous to change either the pendant alkyl chain length of the exchanger or to alter the electronic environment around the  $\text{P} \begin{array}{l} \text{=O} \\ \text{<O}^- \end{array}$  exchange group. In the first instance, a lengthening of the pendant chain might enable greater steric mobility of the ion exchange site and might also induce some plasticisation (mediation) within the polymer. Alternatively, the change of exchange site from a phosphate to e.g. a phenylphosphonate will alter the electronic environment around the  $\text{P} \begin{array}{l} \text{=O} \\ \text{<O}^- \end{array}$  group and bring about changes in the relative ionic affinity of the sensor group. The effect of the different monomer systems upon the ultimate polymer matrix may, however, nullify or complicate any of the above effects.

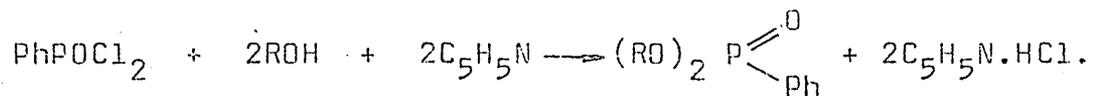
Two suitable alcohols were available which would extend the pendant alkyl chain - oleyl alcohol and 10-undecen-1-ol (w-undecenol). The w-undecenol system might be expected to allow greater flexibility of the sensor group and would resemble the didecylphosphate group used in earlier Ca ISE. Oleyl alcohol, whilst not terminally unsaturated, would give rise to a C<sub>8</sub> pendant alkyl chain on the sensor in addition to another C<sub>8</sub> n-alkyl chain. The presence of this additional C<sub>8</sub> chain might modify the polymer matrix to an unknown extent.

Whilst feasible to prepare these materials, the following points must be borne in mind with regard to the polymerisation of such organophosphorus monomers<sup>166</sup>:

- 1) esters with one allyl group can either be converted into relatively low molecular weight (MW) polymers or, more usually, they cannot be polymerised at all;
- 2) certain esters with pentavalent P, or with 2 or 3 allyl groups are capable of giving high MW compounds with reticulated structures which are infusible and insoluble in organic solvents, (i.e. crosslinked);
- 3) allyl esters of P with any number of unsaturated groups can take part in copolymerisations;
- 4) an increase in MW of an ester monomer (all other things being equal) lowers its capacity for polymerisation.

Thus, copolymerisations with di- or trifunctional monomers would appear favourable, but the high MW of the w-undecenyl and oleyl systems discussed above may result in difficult polymerisation

The use of dialkylphenylphosphonate was made to change the electronic environment around the sensor group. This material is synthetically available using the reaction below.



Whilst not commercially available, it has been prepared<sup>167,168</sup> and its ability to polymerise and copolymerise has been demonstrated.<sup>169,170,171</sup> Thus, providing the new sensor monomers could be produced and subsequently copolymerised then the effect of making changes in the ion-exchange site environment could be investigated. In particular any changes in selectivity of the subsequent electrodes should give an insight into response of a CBS electrode.

## 4.2 Experimental

### 4.2.1 Trioleyl phosphate, (TOP)

Oleyl alcohol (38g, 0.14 mole), pyridine (11.2g, 0.14 mole) and dry toluene were placed in a 500cm<sup>3</sup> 3-necked flask equipped with a mechanical stirrer, a condenser and a dropping funnel. A blanket of dry nitrogen was maintained within the flask. The temperature of the flask and contents was reduced to around -5°C using an ice/salt bath, and redistilled phosphoryl chloride (7.24g, 0.047 mole) was then added to the rapidly-stirred flask contents over a period of two hours. At the end of this time the temperature of the flask was allowed to rise to ambient and the mixture refluxed for two hours. Turbulent stirring was continued such that the pyridine hydrochloride precipitate was kept in suspension. After 2 hours, the reaction mixture was cooled and pyridine hydrochloride filtered off. Toluene was removed under reduced pressure and the product, a viscous slightly yellow oil, was evacuated at 40-50°C overnight to remove traces of toluene and pyridine.

Attempted distillation of this oil at 240°C and 0.1 mm Hg resulted in decomposition. However, chemical and spectroscopic analysis showed that the product was of sufficient purity to be used for membrane production.

#### Infra red (IR) spectroscopy

cm<sup>-1</sup> : 3010(sh, C-H str., alkene); 2920, 2850(C-H str., aliphatic);  
1660(w, C=C str.); 1470(C-H def.); 1260(P=O); 1020(C-O-P).

$^1\text{H}$  nuclear magnetic resonance (nmr) spectroscopy.

$\text{CDCl}_3$ ,  $\delta$  (ppm): 0.90 (s, 9H) ( $-\text{CH}_3$ ); 1.35 (s, 66H) ( $-\text{CH}_2$ );  
1.75 (s, 6H) ( $\text{CH}_3-\text{CH}_2$ ); 2.08 (d, 12H) ( $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2$ );  
3.4-4.4 (m, 6H) ( $\text{CH}_2-\text{O}-\text{P}$ ); 5.4 (t, 6H) ( $-\text{CH}=\text{CH}-$ )

Thin layer chromatography (TLC)

20% v/v ethyl acetate in 60-80°C Petroleum ether:

Major spot,  $R_f = 0.68$ ; Trace spots,  $R_f = 0.34$ ; negligible,  
 $R_f = 0.21$  (oleyl alcohol).

Phosphorus analysis

P(found) = 3.52%

P(calc.) = 3.66%.

4.2.2 Tri(10-undecenyl) phosphate (TUP)

Redistilled phosphoryl chloride (15.33g, 0.1 mole) was added to 10-undecen-1-ol (51.09g, 0.3 mole) and pyridine (23.7g, 0.3 mole) in 150  $\text{cm}^3$  of 40°-60°C petroleum ether. Pyridine hydrochloride was filtered off and the solvent removed under reduced pressure. The resulting clear liquid was exhaustively evacuated to remove final traces of solvent and pyridine. This material was used without further purification.

IR spectroscopy.

$\text{cm}^{-1}$ : 3080 (C-H str., alkene); 2920, 2850 (C-H str., aliphatic);  
1635 (C=C, alkene), 1280 (P=O str.); 1015 (C-O-P str.)

$^1\text{H}$  nmr spectroscopy.

$\text{CDCl}_3$ ,  $\delta$  (ppm): 1.30 (s, 42H) ( $-(\text{CH}_2)_7-$ ); 2.08 (d, 6H) ( $\text{CH}_2\text{CH}.\text{CH}_2$ );  
4.1 (q, 6H) ( $\text{CH}_2-\text{O}-\text{P}$ ); 4.75-6.1 (m, 9H) ( $\text{CH}_2=\text{CH}-\text{CH}_2$ )

TLC 50% Ethyl acetate/Petroleum ether:

Major spot,  $R_f = 0.6$ ; minor constituent  $R_f = 0$ ; negligible  $R_f = 0.46$  - (10-undecen-1-ol).

Phosphorous analysis

P(found) = 5.70, 5.64%

P(calc.) = 5.60%.

4.2.3 Diallyl phenylphosphonate (DAPP)

Redistilled allyl alcohol (23.24g, 0.40 mole), pyridine (31g, 0.39mole) and (150cm<sup>3</sup>) ether(petroleum) were stirred rapidly in a 3-necked 500cm<sup>3</sup> flask maintained at around -5°C. Phenylphosphonic dichloride (45g, 0.2 mole) was added slowly to the mixture over a 2 hour period. The mixture was refluxed for 2 hours and then left overnight, with stirring, to cool. Filtration of the pyridine hydrochloride and evaporation of the solvent yielded a slightly yellow liquid (28g, 85%). Distillation of this crude material (107 to 108°C, 2.5x10<sup>-2</sup> mm Hg) yielded a clear colourless distillate.

IR Spectroscopy

cm<sup>-1</sup>: 3080(C-H str., alkene); 1660(C=C str. alkene); 1605 (C=C str., aromatic); 1430(P-Aryl); 1255(P=O); 1000 (P-O-C str./P-phenyl).

<sup>1</sup>H nmr spectroscopy

CDCl<sub>3</sub>,  $\delta$  (ppm): 4.4-6.4(m, 10H) (allylic protons)  
7.3-8.1(m, 5H) (phenyl protons)

### Mass spectra

m/e : 238 ( $m^+$ ), 197( $m^+ - 41$ , loss of  $\text{CH}_2=\text{CHCH}_2^-$ )  
181( $m^+ - 57$ , loss of  $\text{CH}_2=\text{CHCH}_2\text{O}^-$ ), 140( $m^+ - 98$ )

### Thin layer chromatography (TLC)

50% Ethyl acetate/Petroleum ether:

Crude material : 2 spots Major,  $R_f = 0.40$

Minor,  $R_f = 0$  (baseline)

Distilled product : 1 spot  $R_f = 0.42$

#### 4.2.4 Membrane preparation.

Membranes were produced by solvent-casting from THF solution as previously described (see 2.3.2). Amounts of monomer and initiator used were 4.5 and 2.5% m/m respectively.

Polymerisations were completed by heating the membranes under vacuum (1 mm Hg) at 50°C. Hydrolysis of membranes so produced was accomplished in 5% m/m methanolic KOH. Electrodes were produced, treated and evaluated as has been previously described (Chapter 3) for the TAP model system.

### 4.3 Results and Discussion.

#### 4.3.1 Membrane electrodes incorporating trioleylphosphate (TOP) monomer.

The production of membranes using TOP monomer generally resulted in the presence of areas of opacity within the membrane. This was indicative of poor or incomplete polymerisation which may have been attributable to the high molecular weight of the monomer (see Section 4.1). Despite this, a membrane containing 4.56% m/m TOP and 2.46% m/m ABIN was successfully prepared. The production of this membrane required 48 hours of UV irradiation but did result in an almost completely clear polymer membrane (M57). Analysis of this membrane for its phosphorus content yielded the results shown below:

##### P Analysis (M57)

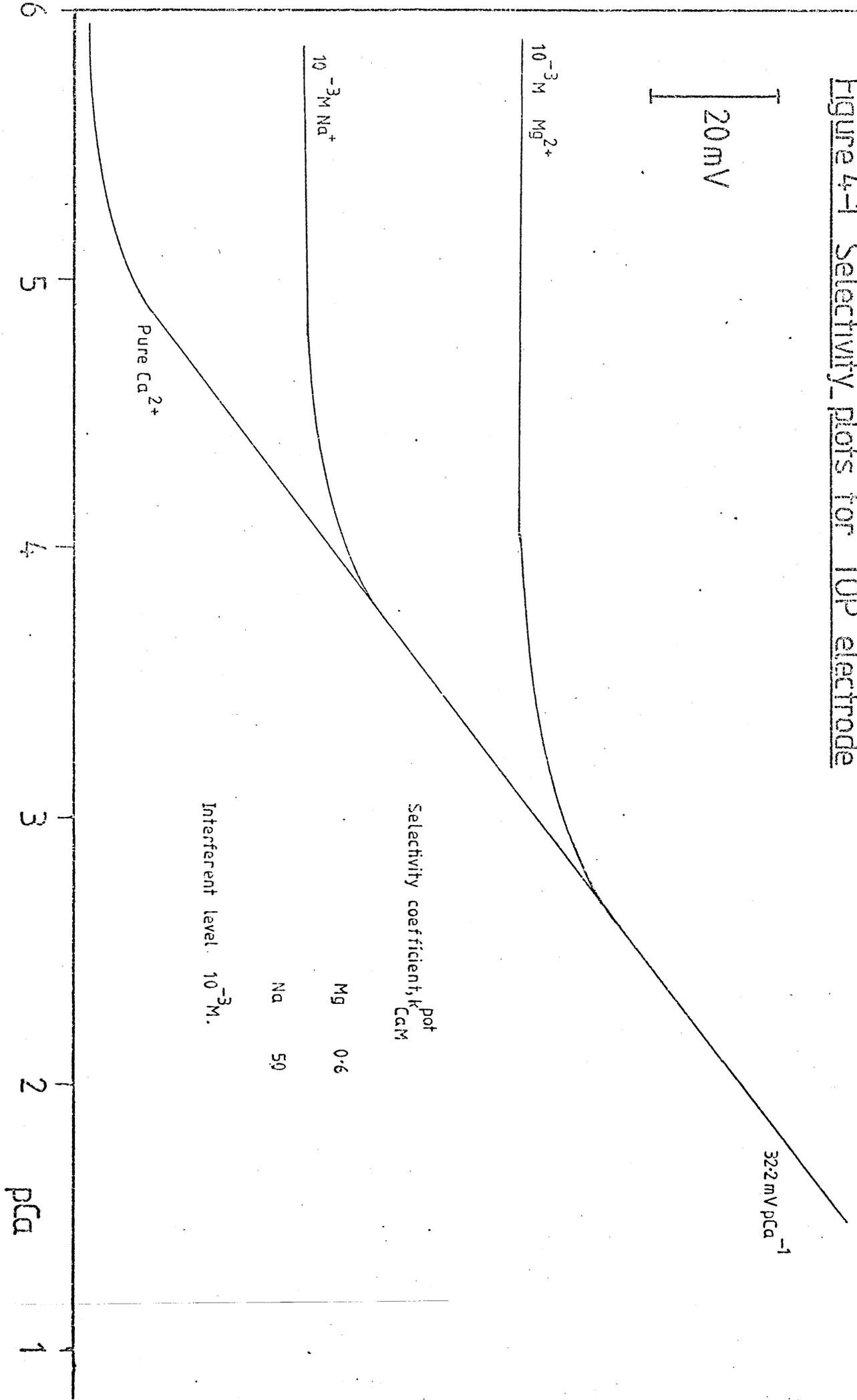
P in the cast membrane=0.195% (P-calc. = 0.156%).

P content of the THF-insoluble fraction=0.136%.

P content of membrane after hydrolysis=0.119%.

These results indicated a high level of TOP incorporation into the membrane. This might have been expected, as TOP, with such a high MW, was highly involatile and would not be lost during casting - unlike TAP. The levels of P remaining after THF attack and hydrolysis indicated a high level of monomer incorporation. Thus, 70% of the monomer in the cast membrane was covalently-bound (i.e. not soluble in THF). The insolubility of the membrane indicated that TOP incorporation was by crosslinking, as intended.

Figure 4-1 Selectivity plots for TOP electrode



Electrodes made from a TOP membrane generally showed sub-Nernstian calibration slopes - usually in the region of + 15 mV.pCa<sup>-1</sup>. However, some electrodes did show a Nernstian response to calcium ion but the slope of these electrodes generally degenerated to a value of + 15 mV.pCa<sup>-1</sup> over a period of 3 to 5 days.

The calibration and selectivity plots of an electrode made from a TOP membrane (M57) are shown in Figure 4-1. The electrode showed a linear calibration over a wide activity range with a limit of detection around  $5 \times 10^{-6} \text{ M Ca}^{2+}$ . Selectivity was in the order;  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{M}^+$ , as has been previously noted for TAP-containing electrodes (Chapter 3). The selectivity shown by such a TOP electrode was slightly poorer ( $k_{\text{CaMg}}^{\text{pot}} = 0.6$ ,  $k_{\text{CaM}}^{\text{pot}} = 50$ ), than for a TAP membrane electrode. The general performance of the TOP electrode was never as good as that of a TAP electrode in terms of precision. This selectivity and overall performance suggested that the use of TOP in a covalently-bound sensor (CBS) electrode was to no advantage. The change in sensor pendant group gave no significant selectivity change and the difficulty of copolymerising TOP led to discontinuation of its use.

#### 4.3.2 Membrane electrodes incorporating tri(10-undecenyl) phosphate (TUP) monomer.

As was the case with membranes using TOP monomer, some difficulty was experienced in copolymerising TUP monomer and SBS. The promotion of complete reaction, indicated by a clear

membrane, generally required up to 36 hours of UV irradiation. As for the TOP system, it might again be concluded that the high MW of the monomer had exerted some retarding effect upon the copolymerisation reaction. Clear membranes, with only occasional small opaque patches, were generally produced. The insolubility of these membranes in THF and the level of 'THF-insoluble' P remaining were taken as firm indications of crosslinking and the covalent incorporation of monomer. Phosphorus analysis of a membrane containing 4.52% m/m TUP and 2.53% m/m ABIN yielded the results below:

P Analysis (TUP membrane)

P in the cast membrane=0.239% (P(calc.) = 0.237%)

P content of THF-insoluble fraction=0.171%

P content of membrane after hydrolysis=0.142%.

These results suggested that there was no significant P loss during the casting process. As with TOP monomer, this was thought to arise from the very low volatility of the high MW monomer. The insolubility of the membrane in THF indicated extensive crosslinking whilst the 'THF-insoluble' P result indicated that 72% of the P incorporated was covalently-bound.

Such a membrane, when hydrolysed e.g. for 1 hour in 5% methanolic KOH, could be incorporated into an electrode body (See 3.2.2) and its response to calcium ions evaluated. An electrode formed thus was calibrated for its response both to pure calcium ions and to calcium in the presence of Mg, K and Na.

mV

Figure 4-2 Selectivity plots for TUP electrode

20mV

0

SLOPE 30.6 MV/DEC

Mg

K

Na

PURE Ca

SELECTIVITY COEFFICIENT,  $K^{POT}$

Mg 1.0

K 110

Na 90

AT  $10^{-3}$  M INTERFERENT

6

5

4

3

2

1

pCa

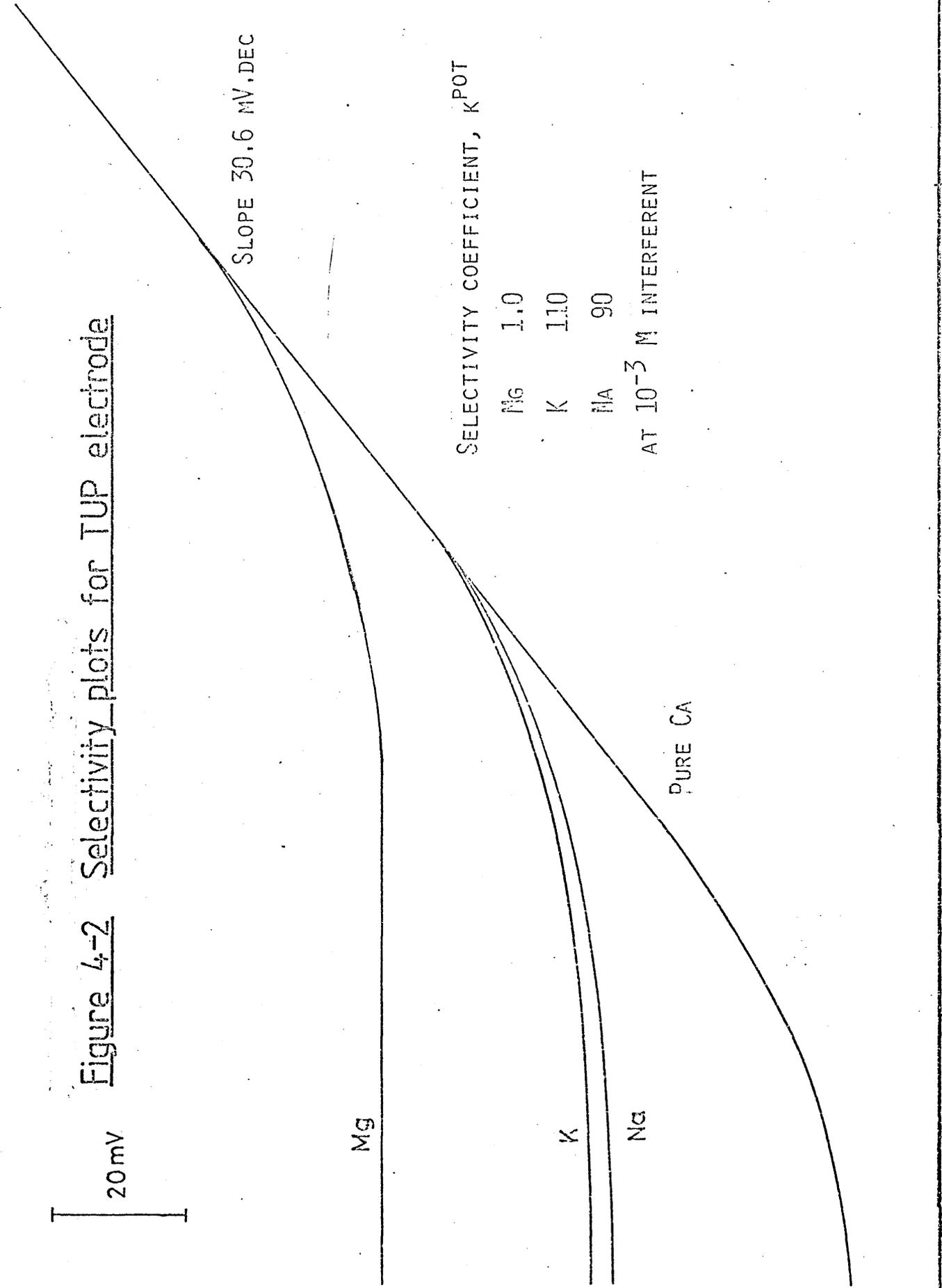
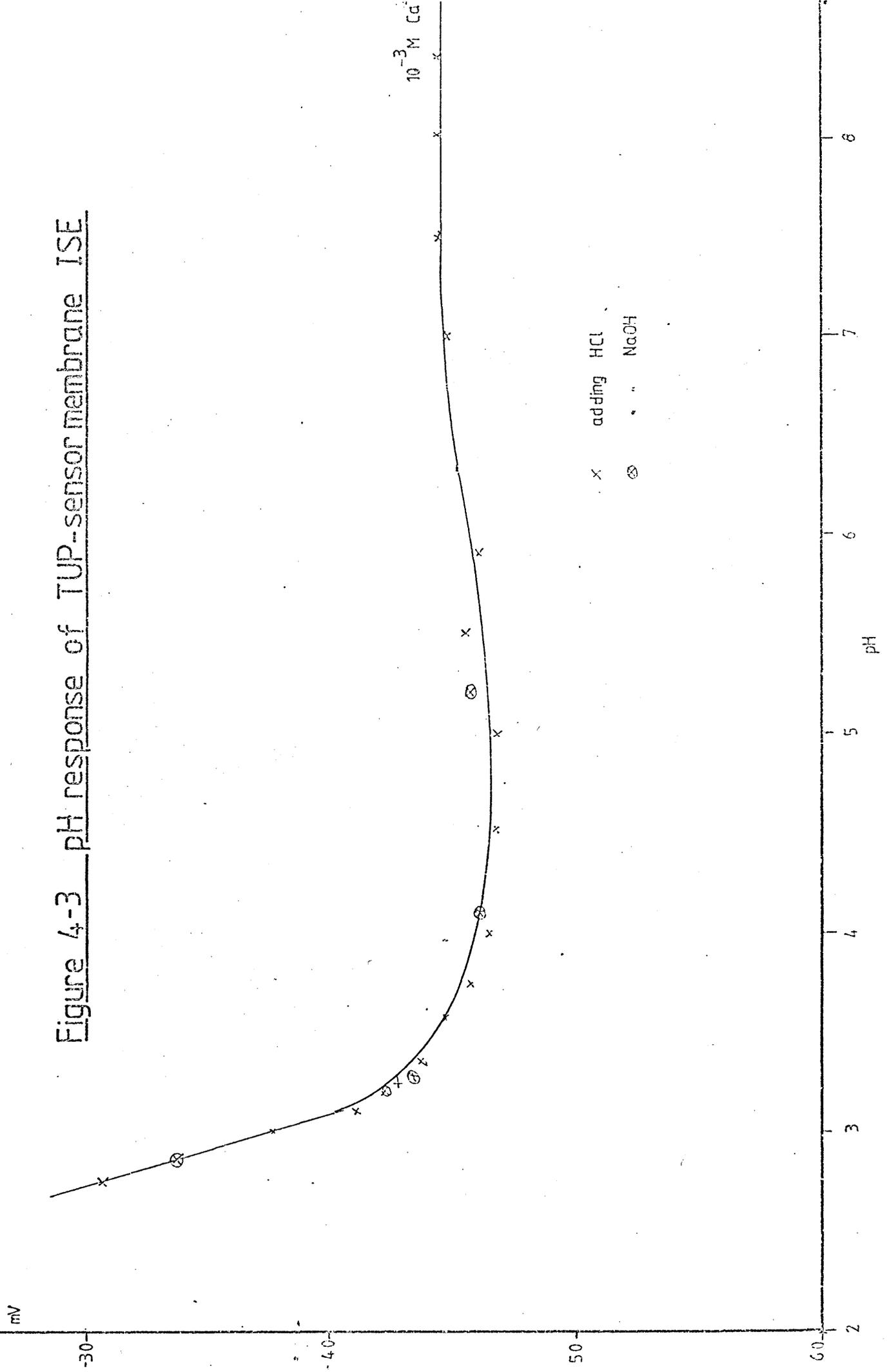


Figure 4-3 pH response of TUP-sensor membrane ISE



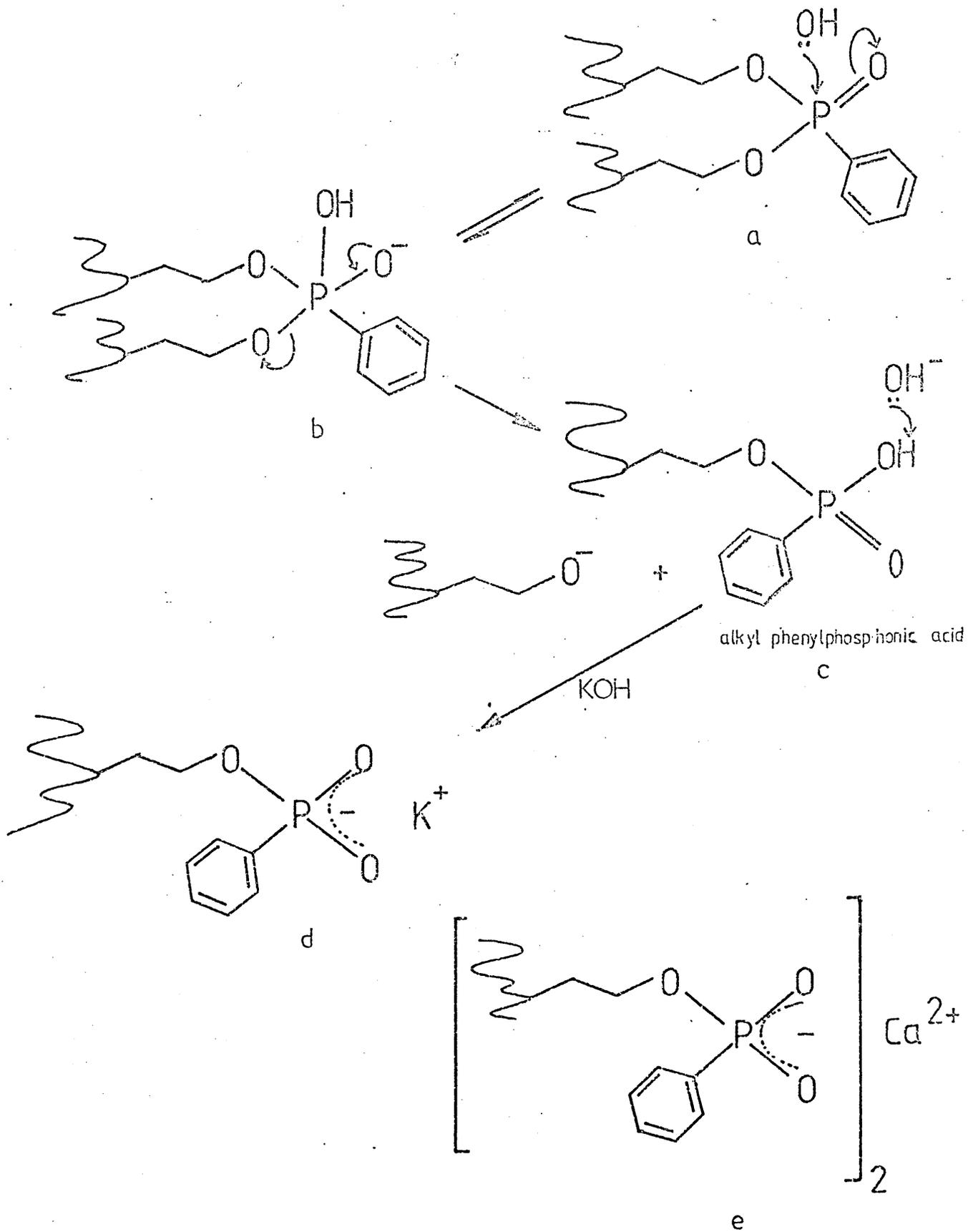
The resulting calibration and selectivity plots (Figure 4-2) indicated a lod of  $5 \times 10^{-6} \text{ M}$  and a selectivity in the order;  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{M}^+$ . Selectivity coefficients,  $k_{\text{CaM}}^{\text{pot}}$ , were generally poorer for this electrode (Mg=1.0, K=110 and Na=90) than for a TAP electrode (Mg=0.3, K=30, Na=27). The pH working range (Figure 4-3) was similar but a very small variation ( $\sim 1 \text{ mV}$ ) was seen over the pH 4-6 range probably due to the less favourable performance of this electrode rather than to a pH effect. It was not thought that this electrode exhibited a pH 'dip' as seen with e.g., the Orion 92-20, as the magnitude of the deviation was so small. Further optimisation of polymerisation and hydrolysis conditions may have yielded an electrode with performance to equal that of a TAP electrode. However, it was not thought that a significant improvement could be made. Thus, there again appeared no advantage to be gained from an increase in the pendant alkyl chain length attaching the sensor group to the polymer skeleton.

#### 4.3.3 Membrane electrodes incorporating diallylphenyl-phosphonate (DAPP) monomer.

This monomer was found to copolymerise easily - as might have been expected from its use by other workers<sup>169</sup>. Reaction times similar to those used for TAP electrodes were used and the membranes so produced were of a high clarity and resilience. The incorporation of the difunctional monomer meant that only two links were made from the sensor to the butadiene polymer (Figure 4-4a). On hydrolysis of this dialkyl phenylphosphonate, a, nucleophilic attack at P occurred forming an intermediate, b,

Figure 4-4

Hydrolysis of a DAPP-containing SBS membrane



which released an alkoxy group to give the monoalkyl phenylphosphonic acid structure, c. In the presence of base (KOH), the phosphonate group would exist as the  $K^+$  salt of the anion, d. Conditioning in  $10^{-1}M$   $CaCl_2$  of a membrane containing this group yielded the calcium form of the exchanger, e.

Production of a membrane of this type was carried out in exactly the same manner as that used for TAP membrane fabrication (Section 2.3.2). Thus, DAPP (4.89% m/m) and ABIN (2.69% m/m) were incorporated into SBS using solvent casting from THF. Membranes so formed were clear and tough but tended to show a 'two-sided' electrochemical response. The membranes were insoluble after casting and P analysis on the membrane gave the results below:

P Analysis

P in cast membrane = 0.44% (P calc. = 0.627%)

P content of THF-insoluble fraction=0.365%

P content of hydrolysed\* membrane=0.077%

\* overnight in 1% methanolic KOH.

These results indicated several points:

- a) there is a loss of P on casting - which has also been seen with TAP but not with high MW monomers (TOP, TUP);
- b) crosslinking again occurs, with a difunctional monomer, and 83% of the monomer was covalently-bound;
- c) hydrolysis of the copolymerised DAPP yields a sensor attached to the polymer by one anchor only. Thus, loss of P on hydrolysis can occur and mild conditions are required.

mV

Figure 4-5 Selectivity\_plots for DAPP electrode

20 mV

SLOPE = 36 mV, DECADE<sup>-1</sup>

Mg

BA

SR

K

NH<sub>4</sub>

NA

PURE CA

SELECTIVITY COEFFICIENT, K<sup>POT</sup>

Mg	2.1	BA	1.05
SR	1.0	K	200
NH <sub>4</sub>	170	NA	130

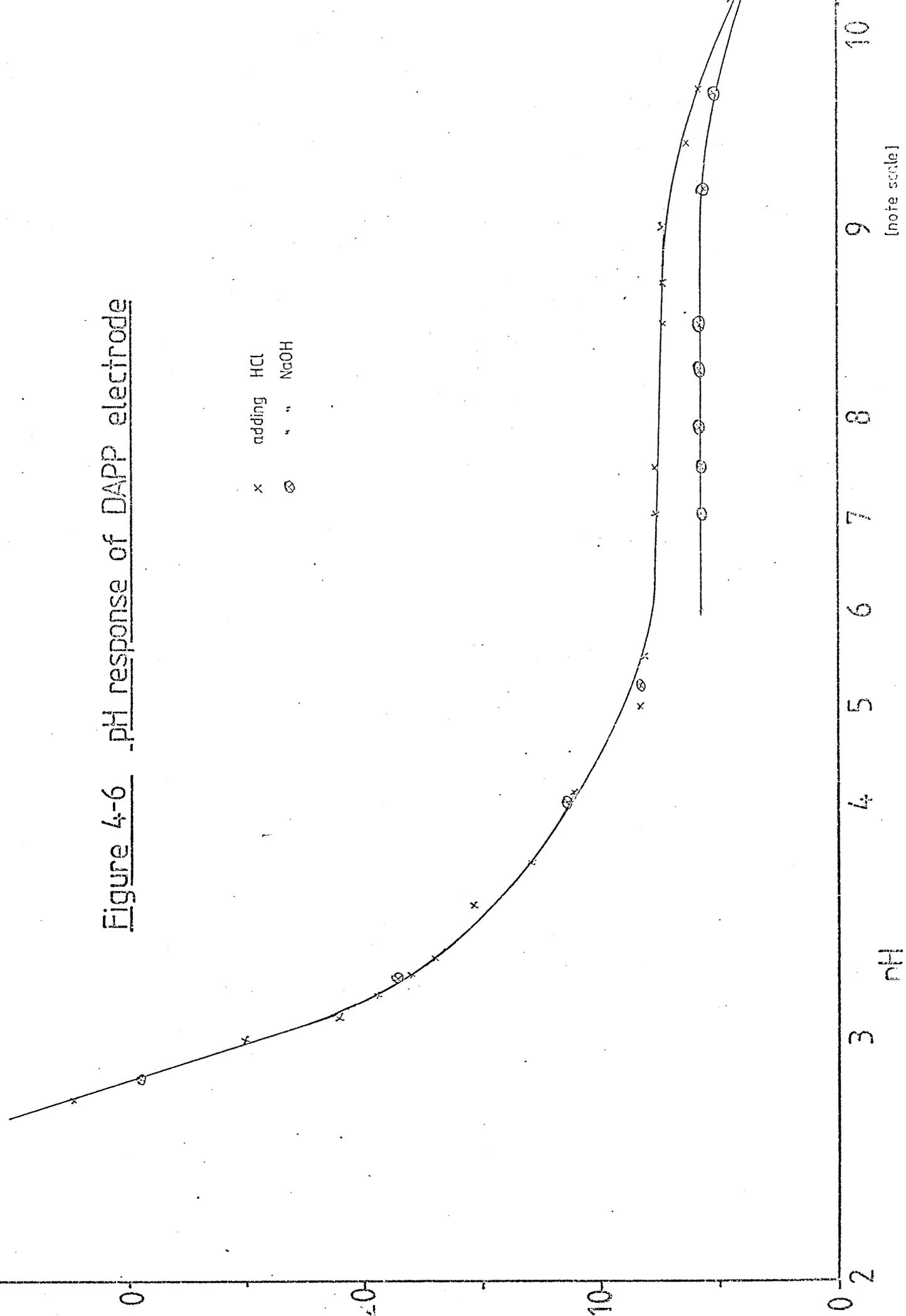
AT 10<sup>-3</sup> M INTERFERENT

1  
2  
3  
4  
5  
6

P CA

Figure 4-6 pH response of DAPP electrode

x adding HCl  
⊗ " " NaOH



[note scale]

Using the required mild hydrolysis conditions (2 hours cold 5% methanolic KOH) DAPP membranes yielded electrodes with slopes usually falling in the 15-25 mV.pCa<sup>-1</sup> range. This observation may have been indicative of too-vigorous hydrolysis. However, electrodes showing Nernstian or near-Nernstian slopes could be produced using mild or short hydrolyses. The calibration and selectivity plots of such an ISE may be seen in Figure 4-5. These plots indicate a lod of around 10<sup>-5</sup> M Ca<sup>2+</sup> with poor selectivity -- particularly for Ca<sup>2+</sup> in the presence of divalent cations. The pH response of a DAPP electrode (Figure 4-6) showed a poorer pH range than for a TAP electrode. The pH independent range ran from 5 to 9 (compared with 4 - 10 for a TAP sensor) and the displacement of the line on addition of NaOH underlined the poor Na<sup>+</sup> selectivity. General analytical behaviour in terms of precision, response time and lifetime was similar to that shown by TAP electrodes. The sensitivity of DAPP to hydrolysis and the poorer selectivity of the DAPP electrode would seem to favour the use of TAP.

It was also noticeable that the DAPP electrodes showed a particularly obvious 'two-sided' effect. That is to say, the electrode response depended upon the orientation of the membrane. This is indicated in Table 4-2 where the effect of orientation reversal is shown. Electrodes 1a and 2a both had the membrane top face (i.e. the upper side in the casting ring) in contact

TABLE 4-2. Effect of membrane orientation on electrode response.

Date Electrode	5/9				10/9			13/9		
	1a <sup>1</sup>	1b	2a	2b	1a	1b	2a	2b	1b	2b <sup>3</sup>
10 <sup>-6</sup> M	-78 <sup>2</sup>	+98	-98	-96	-83.6	+109	-94	+118	+119	-44.6
10 <sup>-5</sup>	-72	"	-84	"	-77.8	"	-78.4	"	"	-37.4
10 <sup>-4</sup>	-57.8	"	-59.8	"	-62.4	"	-57.6	"	"	-29.5
10 <sup>-3</sup>	-38.8	"	-38.8	"	-41.8	"	-35.8	"	"	-22.4
10 <sup>-2</sup>	-22.8	"	-24.6	"	-25.8	"	-20.2	"	"	-13.8
2x10 <sup>-2</sup>	-15.4	"	-19.5	"	-21.8	"	-16.8	"	"	-11.8
10 <sup>-1</sup>	-3.8	"	-4.6	"	-12.4	"	+0.4	"	"	-

1. 58.1a top face to int.reference solution.

2a " " " "

1b bottom face to int.reference solution.

2b " " " "

2. All readings in mV.

Note 3: only 2b inverted.

with the internal reference solution (IRS). Electrodes 1b and 2b had the top face contacting the test solution. As can be seen (Table 4-2) electrodes 1a and 2a with the top face to the IRS gave functional ISE - albeit with a reduced calibration slope. However, electrodes 1b and 2b showed no response to  $\text{Ca}^{2+}$  ions even after extended conditioning. Having established these responses, the membrane of electrode 2b was carefully cut away from the PVC sensor body. This membrane was then inverted and re-stuck to the sensor body. On calibration of electrodes 1b and 2b, 1b remained non-responsive whilst 2b showed a definite response to  $\text{Ca}^{2+}$  ions. Although the calibration was sub-Nernstian, it indicated that a response could only be obtained from this particular membrane when it was mounted in a particular configuration.

This 'two-sided effect' has also been noted for membranes incorporating TAP. Thus an electrode mounted with the upper side of the cast membrane contacting the test solution showed either no  $\text{Ca}^{2+}$  calibration slope or a slope which never exceeded  $15 \text{ mV.pCa}^{-1}$ . Nernstian, or near-Nernstian response was only obtained with the top face contacting the internal reference solution. Similar behaviour has also been noted for PVC matrix calcium electrodes (ref.132, p.95) where electrodes with the top face to the test solution yielded slopes of only  $+14 \text{ mV.pCa}^{-1}$ . Similar effects may be taking place in both these instances. Evaporative loss from the upper membrane surface and chromatography of components into the lower regions of the membrane (which will be solvent rich) may result in a

non-homogeneous vertical distribution, with site depletion at the top surface. This depletion of the top layer may be even worse with TAP and DAPP due to the formation of the 'skin' during polymerisation. This 'skin' may prevent diffusion of the TAP/DAPP into the upper surface layer yielding a top surface almost devoid of monomer and, thus, <sup>o</sup>in exchange sites. It may be deduced that volatile loss of monomer plays a significant role as when this loss is not as marked, e.g. using involatile monomers TOP and TUP, the 'two-sided effect' is much less evident.

If the side of the membrane (the top side) with little or no monomer/sensor is mounted in contact with the test solution, then there will be no sensing of  $\text{Ca}^{2+}$  activity and, therefore, no electrode response. If there is a limited number of sites, then it might be expected that some response will be seen. However, the response may be drastically sub-Nernstian and this has been seen for both PVC and TAP membranes. If, on the other hand, the membrane side with no sensor is placed in contact with the internal reference solution, it may still act as a reference surface. Thus, there will be no potential change at the internal reference interface (as required) but changes will occur, and will be detected, at the test solution interface because that side contains sensor sites. In addition to the volatilisation and chromatographic effects already mentioned, there may be some morphological differences between the two sides. Different pore sizes have been seen on the two sides of

PVC membranes and different polymer densities may be seen on the sides of a TAP membrane. These differences may further affect the electrode response, but volatile loss would seem to be the major effect with TAP/DAPP membrane electrodes.

#### 4.4 Conclusions.

It has been demonstrated that, in addition to the use of TAP, other organophosphorus monomers may be incorporated into a polymeric matrix to yield sensor groups for CBS electrodes. Thus, TOP, TUP and DAPP may be utilized such that either the pendant chain length or electronic environment of the sensor is modified. Electrodes made using these monomers showed high levels of copolymerisation and yielded covalently-bound sensor membranes. Although electrodes using these membranes showed, in many cases, Nernstian calibration slopes, their selectivity compared to TAP electrodes was not improved. In most cases the selectivity was slightly worse. In addition, some retardation of the polymerisation when using the higher MW monomers was experienced. Thus, there appeared no benefit from lengthening the alkyl chain. This was, perhaps, to be expected, as when the phosphate group is bound to the polymer, the pendant chain becomes extremely long anyway. The alteration of the exchanger from a dialkyl phosphate to a monoalkyl phenylphosphonate did not improve selectivity either. This may have been a consequence of the comparatively stronger complexes formed by the more acidic phosphonic acid group. The use of DAPP also resulted in loss of monomer by volatilisation during casting in much the same way as for TAP monomer. Of the electrodes produced so far,

TAP seemed to give the best overall performance and had also been the most-optimized. Such an electrode might usefully be investigated to assess whether its lack of selectivity would be an insuperable barrier to the electrode's analytical application.

CHAPTER 5.

Applications of a covalently-bound  
sensor electrode.

5.1 The use of triallyl phosphate (TAP) in a covalently-bound sensor (CBS) electrode has yielded an electrode showing high durability and excellent general analytical performance. Modification of this sensor group by changing either the pendant alkyl chain length or the sensor group has been shown to exert little effect on electrode selectivity. Thus, the analytical utility of TAP membrane electrodes might usefully be assessed. Care was necessary, however, in the application of such an electrode, as the electrode selectivity for  $\text{Ca}^{2+}$  over other divalent cations was not as good as seen with some commercially-available electrodes. This shortcoming in selectivity might, in some instances, be of little consequence when weighed against the possible advantages to be gained from the use of a CBS electrode.

Firstly, an investigation into the analysis of water hardness (Ca + Mg) by a less-selective CBS electrode might be useful. A CBS/TAP electrode with poor  $\text{Ca}^{2+}$  over  $\text{Mg}^{2+}$  selectivity might usefully be used for such a determination. The ease and speed of analysis would be important and a long lifetime sensor might enable long-term on-stream monitoring of water hardness. The CBS electrode was also evaluated for its ability to monitor a coking oven effluent and its effect on a receiving stream. Such monitoring is very important in the South Yorkshire/North Derbyshire area due to the relatively large number of coking plants, most of which discharge to small and easily-polluted streams. One approach to the monitoring

TABLE 5-1.

Analysis of the effluent from a coking plant.  
treatment works.

pH 6.9

PERMANGANATE VALUE 750 ppm

CHEMICAL OXYGEN DEMAND 500-1000 ppm

DISSOLVED OXYGEN 50% Saturated

PHENOLS 225 ppm CNS<sup>-</sup> 235 ppm

NH<sub>3</sub>-N 176 ppm

Ca 2690 ppm

Mg 110 ppm

of such an effluent and stream was investigated, where a CBS electrode was used to monitor calcium levels in various samples. This use of calcium as a tracer is made possible by the use of lime in the coking plant effluent treatment works. This use of lime  $\text{Ca(OH)}_2$  results in an effluent which contains a high concentration of calcium. Thus, calcium forms the major ionic constituent of a coking plant effluent but, in addition to this, there are many other components (Table 5-1) many of which might interfere with or cause deterioration of a calcium ISE. Ions such as  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{NH}_4^+$  could be present in the effluent and if there in relatively large quantity, will cause interference with the calcium electrode response. In addition, the effluent is heavily loaded with phenolic compounds of many types and may also contain organic compounds which show surfactant behaviour. There are various ISE techniques which might be used for the potentiometric determination of  $\text{Ca}^{2+}$  ions in such an effluent or of  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  ions in water.

#### 5.1.1 Direct Potentiometry.

This is the simplest of all electrode techniques and is analogous to the well-established use of a pH electrode. Thus, a reference/ion-selective electrode pair is placed in solutions of the determinand ion, e.g.  $\text{Ca}^{2+}$ , over the range required and a calibration graph of observed cell potential (mV) against  $\log a_{\text{Ca}^{2+}}$  is constructed. The electrode pair is then immersed in the test solution and the resulting potential is related to the determinand activity by means of the above calibration

graph. Knowledge of the determinand activity coefficient enables conversion of the sample determinand activity to concentration. Although the simplest and, consequently, most rapid of the various potentiometric techniques, the direct method is also subject to the largest errors. In particular, uncertainty in the ionic strength and the activity coefficient may lead to spurious results. This problem is often eliminated by maintenance of a constant ionic strength which will also tend to stabilise the liquid junction potential. Thus, an excess of an inert salt, which does not interfere with the ISE response, may be added to the sample and standard solutions. Use of this approach yields a plot of electrode potential against ionic concentration as the activity coefficient is stabilised, albeit at a low level. In addition to the stabilisation of  $\gamma_{Ca^{2+}}$ , use may be made of pretreatment to control pH, to remove interferent ions, or to match sample and standard matrices. Such an ionic strength adjustment buffer (ISAB) is often used. It must be borne in mind that use of such a buffer must maintain the same degree of complexation of the primary ion as only the free (uncomplexed) ionic species will be sensed by an ISE. Buffers for calcium ion determination have been suggested<sup>76,82</sup> and the use of matrix matching is of great benefit with matrices such as serum and sea-water.

The advantages of this technique are its simplicity and speed and its ability to be used continuously to monitor a stream. Precision, however, is frequently in the range  $\pm 5-10\%$  rsd

and other measurement techniques must be employed if improved precision is required.

### 5.1.2 Standard (or known) Addition.

In this method the electrode set is immersed in a volume ( $V_x$ ) of sample solution and the change in electrode equilibrium potential ( $\Delta E/mV.$ ) noted after addition of a known increment of determinand ions ( $V_s$ ). This method determines total determinand concentration ( $C_x$ ) by application of the equation below:

$$C_x = \frac{C_s V_s}{10^{\Delta E/s} (V_s + V_x) - V_x} \quad s = \text{electrode slope} \\ \text{mV. } \mu\text{X}^{-1}.$$

This equation may be simplified if the volume change on standard addition is very small. The technique and the above equation may be modified to allow analysis by standard subtraction (by use of a complexing or precipitating agent) or by sample addition. A potential change ( $\Delta E$ ) of 5 to 20 mV is a useful value and the use of a multiple standard addition may be made in order to improve precision.

For the production of meaningful results, the following points must be borne in mind:

- a) the activity coefficient must remain constant;
- b) the degree of complexation of the determinand ion must be constant;
- c) a Nernstian calibration is assumed;
- d) the liquid junction potential remains constant;
- e) there must be no interferent present.

The use of pretreated samples may be used to assure points a, b and e above and also to maintain a stable liquid junction potential. The assumption of a perfect Nernstian slope, however, may lead to a significant error and ISE users would be well-advised to establish the actual electrode calibration slope. The use of the standard addition technique permits greater precision than direct potentiometry, but the increase in analysis time and effort may be a disadvantage.

### 5.1.3 Gran's Plots.

This technique is, in effect, an extension of the above standard addition to a multiple standard addition with linearisation of the results. Thus, the Nernst equation:

$$E = E_0 + s \log a_{Ca^{2+}}$$

may be modified such that:

$$10^{E/s} = \text{constant} \times a_{Ca^{2+}}$$

and a plot of  $10^{E/s}$  against  $a_{Ca^{2+}}$  will yield an intercept on the abscissa corresponding to the original sample concentration,  $C_x$ . The use of several additions enables a better precision than with a single standard addition although the calculation and volume corrections necessary make the method lengthy. These disadvantages may be overcome by the use of a simple computer program or by the use of volume-corrected Gran's Plot Paper

(Orion Research Inc.). Such paper acts as a suitable format for the plotting of results graphically and eliminates the need for the rather lengthy calculations otherwise required.

#### 5.1.4 Potentiometric titrations.

This technique is capable of giving the highest precision of an ISE technique, but it is also the most time-consuming. The method is, however, suitable for automation, which may remove both operator error and tedious experimentation. In the case of calcium ion, a calcium ISE/reference electrode couple is placed in the sample solution and the calcium ions are titrated using the electrodes to detect the end-point. Thus, calcium ions are titrated with, and complexed by, EDTA under suitable pH conditions. As calcium ions are complexed, the electrode pair potential drops as the ISE will sense only the free  $\text{Ca}^{2+}$  content. Plotting the observed potential (or the first or second derivative thereof) against the volume of titrant yields a characteristic graph (Figure 5-1) showing a sharp decrease of  $E_{\text{cell}}$  (and hence,  $a_{\text{Ca}^{2+}}$ ) at the equivalence point. The equivalence point may be determined by the use of a Gran's plot technique which relies upon results away from the equivalence point. This latter method is, in effect, a linearised multiple analyte subtraction/standard addition. For a more in-depth account of the basic practice of ISE methodology the reader is referred to recent publications covering this area<sup>172,173,17</sup>

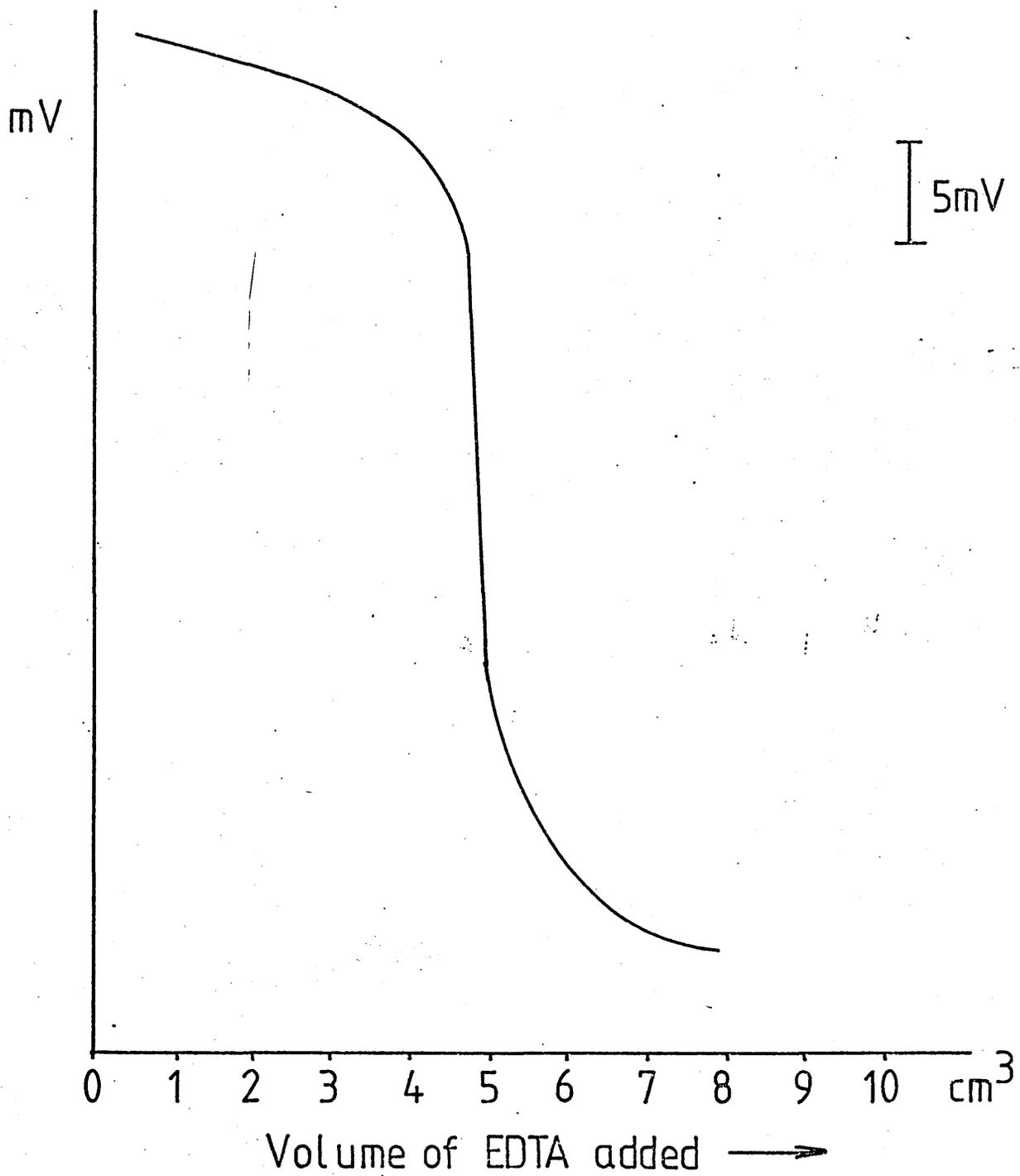


Figure 5-1 Curve from the potentiometric titration  
of Ca(5cm<sup>3</sup> · 0.01M) with EDTA (0.01M)  
using a Ca ISE

Any of the foregoing techniques may be used for the determination of calcium in coking oven effluents with a CBS electrode. The use of direct potentiometry would be particularly advantageous as this method would allow rapid analysis with maximum simplicity. This would be of immense use in a field-monitor as it would enable rapid on-site analyses, albeit with a precision of around  $\pm 10\%$ . This precision, though, may be relatively unimportant when doing a survey on plant or effluent as speed and convenience may be of greater value. Any results requiring further investigation could be verified in the laboratory using a grab sample. Thus, for the monitoring of coking oven treatment plant effluents and receiving streams, a robust electrode in conjunction with a convenient and rapid method would hold many advantages over more traditional methods.

## 5.2 Experimental.

### 5.2.1 Electrodes.

One reference electrode was used throughout:

Corning 47606700M double junction silver-silver chloride reference electrode containing an inner filling solution of 4M KCl and a bridge solution of 1M  $\text{KNO}_3$  in conjunction with the meters previously listed (Section 3.2.4).

Three calcium ISE were used:

- a) Orion 92-20 using Orion 92-20-02 liquid ion exchanger and set up as described in the makers' instruction manual.
- b) PVC calcium ISE - made from PVC powder and Orion 92-20-02 liquid ion exchanger as described by Craggs et al<sup>73</sup>.

c) CBS electrode - produced using 5% TAP as described previously (Chapter 3).

### 5.2.2 Measurement techniques.

For direct potentiometry, the electrodes were first calibrated in pure calcium chloride solution and then the electrode potentials were measured in the sample solutions. Three types of sample were taken; the river above the outfall; the effluent outfall itself; and the river 100m downstream of the outfall. In order to keep samples in a similar range, the effluent and the stream below the outfall were diluted (100x) to bring their calcium activity close to that of the river above. This ensured matching of samples and meant that, providing  $\text{Ca}^{2+}$  ions were the major ionic component, the activity coefficient ( $\gamma_{\text{Ca}^{2+}}$ ) was similar for all samples. Thus, in the absence of any sample pretreatment (other than dilution), an assumption that the ionic strength and, hence, the calcium ionic activity coefficient were determined only by the calcium activity was made. The validity of this assumption would depend upon the presence of ions other than  $\text{Ca}^{2+}$  and would be reflected by any bias in the results obtained. It was borne in mind that any interfering cations would not only affect the electrode potential, but would also influence  $\gamma_{\text{Ca}^{2+}}$  by changing the ionic strength of the analyte solution.

For the standard addition method, aliquots of 0.1 or 1 Molar  $\text{CaCl}_2$  solution were added to the diluted sample and the potential change noted. Calcium calibration slopes were determined for each

electrode so that no error arose from the assumption of a perfectly Nernstian slope. As for the direct method, dilution was the only sample pretreatment used. Gran's plots were constructed on Gran's Plot 10% Volume Corrected Paper (Orion Research Inc.). All analyses were carried out at  $25 \pm 0.5^{\circ}\text{C}$ .

### 5.2.3 Non-potentiometric methods.

In order to ascertain the validity of the calcium results produced using ISE, three independent methods of analysis were used. In addition, magnesium was determined in order to determine whether any interference would be detectable in the electrode methods.

#### 5.2.3.1 Complexometric titration.

An aliquot of sample in a  $100\text{cm}^3$  conical flask was diluted to  $40\text{cm}^3$  with water. Molar NaOH ( $10\text{cm}^3$ ) and 3 drops of Eriochrome Blue-Black R (sodium 1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulphonate) indicator (Hopkin and Williams, Essex) solution (0.2g in  $50\text{cm}^3$  Methanol) were added. The calcium content of this solution was then determined after titration with 0.01M EDTA solution to a pure blue end-point.

#### 5.2.3.2 Atomic Absorption Spectroscopy (AAS)

Flame AAS was used for the determination of both calcium and magnesium using a Pye Unicam SP 90 AA (Pye-Unicam, Cambridge) spectrophotometer under the following operating parameters:

Air/C<sub>2</sub>H<sub>2</sub> flame, single slot (10cm) burner.

Gas flows : Air 5 l.min<sup>-1</sup>.

C<sub>2</sub>H<sub>2</sub> 1.3 l.min<sup>-1</sup>.

	Calcium	Magnesium
Wavelength	422.7nm	285.2nm.
Lamp Current	6 mA	5 mA

Due to the high sensitivity of the 285.2 nm Mg line, the burner was rotated 30°. A 1000 mg.l<sup>-1</sup> background of Sr was used as ionisation suppressor with all calcium standards and solutions. Calibrations for both elements were linear in the 0 to 10 mg.l<sup>-1</sup> range.

#### 5.2.3.3 Atomic emission spectroscopy (AES)

Samples and standards were analysed using AES and an inductively-coupled plasma emission source. A Radyne R50P generator (Radyne, Wokingham, Surrey), a Jarrell-Ash monochromator and a pumped concentric nebuliser were used under the operating conditions below:<sup>177</sup>

Calcium 396.847nm line.

All argon plasma	Injector gas flow	0.37 l.min <sup>-1</sup> .
	Plasma " "	10.5 l.min <sup>-1</sup> .
	Coolant " "	4.5 l.min <sup>-1</sup> .
	Viewing height	22 mm above load coil.
	Power	0.49 kW.

The linear calibration range extended to 500 mg.l<sup>-1</sup> Ca, but the range 0-10 mg.l<sup>-1</sup> Ca was expanded for use here.

#### 5.2.4. Water Hardness (Ca + Mg) analyses.

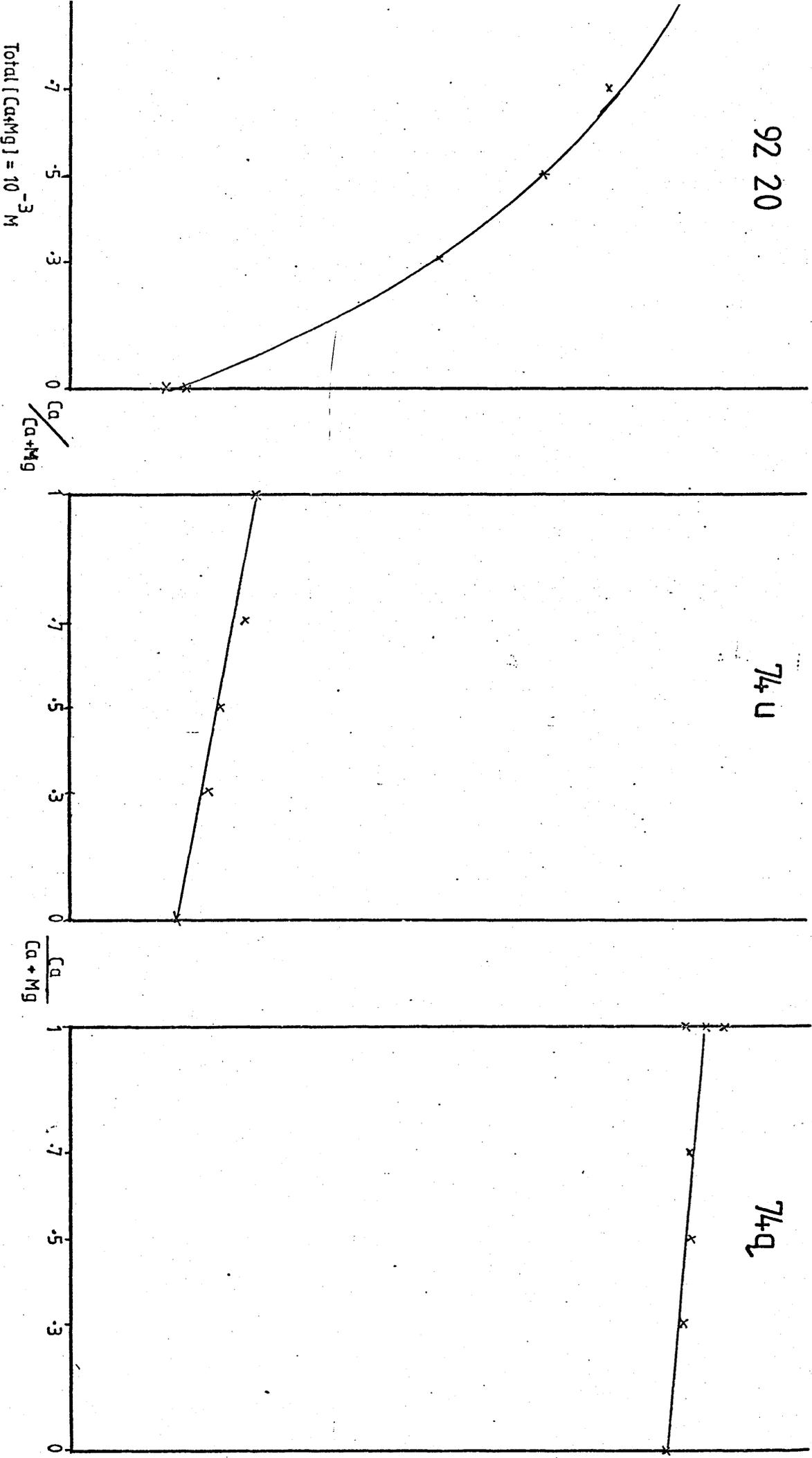
Direct potentiometry was used, in conjunction with two ISE - Orion 92-20 and a CBS electrode, and a single Ag/AgCl reference electrode (See 5.2.1). Combined Ca + Mg were determined by complexometric titration with EDTA. The indicator used was Eriochrome Black T and the solution was buffered to pH 10 with ammonia-ammonium chloride buffer.

### 5.3 Results and Discussion.

#### 5.3.1 Water Hardness determinations.

Water hardness is a measure of the combined concentrations of calcium and magnesium in water. It is usually expressed as  $\text{mg}\cdot\text{l}^{-1}$   $\text{CaCO}_3$  and is a frequently-determined parameter throughout the water supply industry. Use has been made of a PVC electrode for water hardness determination. Thus, a reduced  $\text{Ca}^{2+}$  selectivity over  $\text{Mg}^{2+}$  may result for a PVC electrode using a dialkylphosphate sensor if decanol is used as solvent mediator (Table 1-7). Such an electrode does, however, maintain divalent over monovalent selectivity. Recently a polymer made from PVC or poly(methylacrylate)(PMA) has been used<sup>178</sup> for water hardness determination, but a true measure of calcium and magnesium was not obtained. As the selectivity of a CBS electrode containing TAP shows limited  $\text{Ca}^{2+}$  over  $\text{Mg}^{2+}$  selectivity, such an electrode was evaluated for use in the determination of water hardness. Thus, the response of both an Orion 92-20 and a CBS electrode in mixed  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  solutions was investigated and compared.

Figure 5-2 Comparison of the response of three electrodes in mixed Ca/Mg solutions



The performance of these electrodes was as shown below:

	Orion 92-20	CBS 74u	CBS 74g
Slope mV.pCa <sup>-1</sup>	31.3	27.2	25.9
k <sup>pot</sup> <sub>CaMg</sub> (10 <sup>-4</sup> M)	0.125	0.4	0.7

These results indicated slightly sub-Nernstian calibration slopes for the CBS electrodes and a marginally better selectivity for the Orion electrode. When the response of these three electrodes was compared in mixed Ca<sup>2+</sup>/Mg<sup>2+</sup> solution (Figure 5-2) it was clearly seen that the Orion 92-20 offered more selectivity than either of the two CBS electrodes. Despite the low Ca<sup>2+</sup>/Mg<sup>2+</sup> selectivity shown by the CBS electrodes, the results indicated that there was a definite, though small, calcium-selective response. This selectivity would lead to a bias in any determination of water hardness and indicated that such an electrode would not yield the true Ca + Mg value. This was similarly concluded for a PMA<sup>178</sup> electrode. The conditioning of a CBS electrode in mixed Ca<sup>2+</sup>/Mg<sup>2+</sup> solution in conjunction with mixed internal reference solutions may yield an electrode with the required Ca + Mg response. Such an electrode, when used with an Orion Ca ISE would enable the determination of Ca + Mg, Ca and Mg (by difference) in water samples.

### 5.3.2 Analysis of a Coking Plant Treatment Works Effluent.

The river above the effluent, the effluent itself and the river 100m below the effluent were sampled. These solutions were analysed for Ca content using three different electrodes,

TABLE 5-2. The performance of three electrodes used for the analysis of calcium in coking plant effluent.

	Slope mV.pCa <sup>-1</sup>	pot k <sub>CaM</sub>	Interferent level(m).
Orion 92-20	30.7	Mg <sup>2+</sup> 0.22 Na <sup>+</sup> 0.38 NH <sub>4</sub> <sup>+</sup> 36 *C <sub>8</sub> TA <sup>+</sup> 1.5x10 <sup>3</sup>	10 <sup>-4</sup> 10 <sup>-2</sup> 10 <sup>-3</sup> 10 <sup>-3</sup>
PVC	28.8	Mg <sup>2+</sup> 0.12 Na <sup>+</sup> 0.60 NH <sub>4</sub> <sup>+</sup> 17	10 <sup>-4</sup> 10 <sup>-2</sup> 10 <sup>-3</sup>
CBS	29.6	Mg <sup>2+</sup> 0.5 Na <sup>+</sup> 7 NH <sub>4</sub> <sup>+</sup> 76 *C <sub>8</sub> TA <sup>+</sup> 100	10 <sup>-4</sup> 10 <sup>-2</sup> 10 <sup>-3</sup> 10 <sup>-3</sup>

\* Octyltrimethylammonium ion.

2 separate electrode methods and 3 independent methods. Thus, an Orion 92-20, a PVC and a CBS electrode were first calibrated in pure calcium solutions and their selectivity for calcium in the presence of various interfering cations was determined (Table 5-2). These results indicated that the selectivity of the three electrodes was not markedly different. This was not due to the CBS electrode used being particularly selective, but was brought about by the generally poor selectivity exhibited by both the Orion and PVC electrode. In particular, the selectivity over  $\text{NH}_4^+$  was poor and the interference shown on the Orion electrode in the presence of octyltrimethylammonium ion ( $\text{C}_8\text{TA}^+$ ) was severe ( $k^{\text{pot}}=1.5 \times 10^3$ ). This overall lack of good selectivity precluded the use of an ionic strength adjustment buffer as none of the electrodes seemed sufficiently inert to high background levels of e.g.  $\text{Na}^+$  or  $\text{K}^+$ . This meant that activity coefficients had to be computed, assuming that the ionic strength was determined by the level of  $\text{Ca}^{2+}$  in the solutions, and then used to convert observed activity to concentration. The generally poor selectivity of the electrodes and the assumptions made in calculating  $\gamma_{\text{Ca}^{2+}}$  meant that it was essential for the level of calcium ions to be much higher than the sum of all other ions, particularly  $\text{NH}_4^+$  and surfactant-like chemicals. The use of independent methods of analysing the Ca content would give an indication as to the validity of the assumptions used in the activity calculations. The selectivity of the Orion and PVC electrodes was similar - as would be expected from electrodes using exactly the same ion-exchanger. It may have been a poor

batch of this exchanger which limited selectivity, although a previous study (Table 3-7) using a different exchanger batch had yielded similarly poor  $\text{Ca}^{2+}$  over  $\text{NH}_4^+$  selectivity. Having evaluated the electrode performances, the samples were analysed using all three electrodes.

#### 5.3.2.1 Direct Potentiometry.

Calibration curves of cell potential (mV) against  $\log a_{\text{Ca}^{2+}}$  were constructed. The potentials of each ISE/reference electrode pair in each sample were then related to calcium ion activities using the above graphs. The activity coefficient,  $\gamma_{\text{Ca}^{2+}}$  corresponding to a pure  $\text{Ca}^{2+}$  solution of the same activity was then computed using the ION program (Appendix 1). The observed calcium activity was then converted to a calcium concentration by use of this computed  $\gamma_{\text{Ca}^{2+}}$  value using:  $C_{\text{Ca}^{2+}} = a_{\text{Ca}^{2+}} / \gamma_{\text{Ca}^{2+}}$ .

The use of such an approach is justifiable when calcium ion is the main ionic solution species and when the samples have all been diluted to an ionic strength such that the activity coefficient is not rapidly changing. Thus, the solutions were diluted into the  $10^{-4}$ - $10^{-3}$  M range so that the activity coefficient was not changing dramatically.

The results for the determination of calcium concentration of the three samples are shown in Table 5-3. From these results it may be seen that all samples were diluted to give an activity in the  $10^{-3}$  M range and therefore each had similar ionic strengths and  $\gamma_{\text{Ca}^{2+}}$  values. The results for calcium concentration in the river above the outfall showed good agreement for all three

TABLE 5-3. Potentiometric analysis of coking plant effluent 1) Direct Potentiometry.

Electrode	River upstream <sup>1</sup>			Effluent <sup>2</sup>			River downstream		
	$a_{Ca^{2+}/M}$	$\gamma$	$[Ca^{2+}]/mg.l^{-1}$	$a_{Ca^{2+}/M}$	$\gamma$	$[Ca^{2+}]/mg.l^{-1}$	$a_{Ca^{2+}/M}$	$\gamma$	$[Ca^{2+}]$
Orion 92-20	$1.9 \times 10^{-3}$	.68	112	$1.09 \times 10^{-3}$	.78	5590	$7.6 \times 10^{-4}$	.79	385
PVC	$1.7 \times 10^{-3}$	.70	97	$6.8 \times 10^{-4}$	.82	3320	$5 \times 10^{-4}$	.83	24
CBS	$1.9 \times 10^{-3}$	.68	112	$6.6 \times 10^{-4}$	.82	3220	$5.3 \times 10^{-4}$	.84	25

- 1. No dilution
- 2. Dilution = 1/100

electrodes. In the effluent, the PVC and CBS gave comparable results, but the calcium concentration sensed by the Orion electrode was very high. Checking of this result yielded a similarly high result. The reason for this abnormally high response may have lain in the erratic response shown by the Orion electrode in the presence of the effluent. Even at the dilutions used (1/100), the effluent still had a deleterious effect on the electrode. This was noticeable with the PVC electrode and both membranes began to first go white and then become discoloured on exposure to the effluent. The CBS electrode showed no such effect. The Orion electrode also registered a high value for calcium in the river below the outfall whilst the PVC and CBS results showed good agreement. Again, the high level of effluent in the stream at this point had a dramatic effect on the Orion response. Thorough washing of the Orion electrode was necessary after use in the effluent in order to return some response stability. The calibration slope, however, remained unaffected. Both the Orion and the PVC electrode showed a shortening of their operational lifetime when used in the effluent. Discolouration of the membrane occurred after 2 or 3 days and both electrodes were of little use after a month of intermittent use in this harsh sample. The CBS electrode seemed unaffected by the effluent.

TABLE 5-4. Potentiometric analysis of coking plant effluent 2) Standard Addition.

3) Gran's Plots.

	River upstream	Effluent	River downstream
<u>2. Standard Addition.</u>			
Orion 92-20	125	3365	2200
PVC	140	5410	3775
CBS	110	3770	2610
<u>3. Gran's Plots.</u>			
Orion 92-20	120	3310	2125
PVC	124	6880	2405
CBS	105	3410	2525

All results expressed as  $\text{mg.l}^{-1} \text{Ca}^{2+}$

### 5.3.2.2 Standard Addition.

Single point standard addition and multipoint Gran's Plots were both used. Gran's Plots were constructed on 10% Volume Corrected Paper and the intercept used to determine the calcium concentration of the original sample. For the standard addition, 2cm<sup>3</sup> of 0.1 M CaCl<sub>2</sub> solution were added to 100 cm<sup>3</sup> of sample and the potential change noted. Knowledge of this potential change ( $\Delta E$ ) and the previously-determined electrode calibration slope enabled the original sample calcium concentration to be determined. The results from using these two methods to determine calcium in the three samples are shown in Table 5-4. As with the direct method, results for the river upstream agreed well, particularly for each electrode. The PVC electrode response was very poor for all the samples using standard addition and was suspected to be caused by the membrane degenerating after exposure to the effluent sample. Thus, the results using the PVC electrode are not very meaningful, but indicate the difficulty of analysing such a hostile effluent solution. Results from the Orion and CBS electrodes are consistent for the effluent sample although the CBS result by standard addition proved to be a little higher. In the river downstream, there was a definite difference between the Orion and CBS result - the latter being higher. Overall, the results seemed consistent with those obtained by the direct method.

The use of potentiometric titrations was not pursued for any of these electrodes as preliminary studies had indicated that very small potential breaks occurred. In many cases, no break was detectable and this was thought to have arisen from the poor  $\text{Ca}^{2+}$  over  $\text{Na}^+$  selectivity of the electrodes. Thus, as  $\text{Na}^+$  was added (from the disodium EDTA titrant) the decreasing calcium ion activity was not detected by the electrode.

#### 5.3.2.3 Comparison of results from different methods.

The results for calcium concentration by the electrode methods were compared against those obtained using other methods of analysis (Table 5-5). As may be seen, the agreement between results obtained by EDTA titration, AAS and AES was excellent. Comparison of the results from potentiometry with these independent results gave mixed success.

In the river above the effluent outfall, results from all the methods were in good agreement. This would suggest that the assumption that the total ionic strength (and hence  $\gamma_{\text{Ca}^{2+}}$ ) was governed by the calcium concentration was valid for the stream. Had the ionic strength been higher than predicted by the  $a_{\text{Ca}^{2+}}$  results (i.e. in the presence of ions not affecting electrode response) then the estimate of  $\gamma_{\text{Ca}^{2+}}$  would have been too high and as  $c = a/\gamma$ , the result for calcium concentration,  $c$ , would have been too low. This was not the case. The Orion electrode gave slightly high results, whilst the CBS electrode

TABLE 5-5. A comparison of the results for calcium in coking oven effluents by various methods.

All results expressed as $\text{mg.l}^{-1}$ Ca.			
Technique/Electrode	River u/s	Effluent	River d/s
EDTA titration	108	2800	2075
AAS	114	2820	2120
ICP/AES	109	2800	2140
<u>Direct potentiometry</u>			
Orion 92-20	112	5590	3850
PVC	97	3320	2410
CBS	112	3220	2525
<u>Gran's Plot</u>			
Orion 92-20	120	3310	2125
PVC	124	6880	2405
CBS	105	3410	2525
<u>Standard Addition</u>			
Orion 92-20	125	3365	2200
PVC	140	5410	3775
CBS	110	3770	2610

showed excellent agreement with the independent methods and between potentiometric methods.

In the effluent, however, none of the electrodes using any technique gave a result in agreement with that of the three independent methods. The results all erred on the high side and, with the Orion and PVC electrodes, response was erratic in the effluent. Rapid deterioration and discolouring of both the electrode membranes were apparent and contact with the effluent had to be minimized. This process was irreversible with the PVC electrode and led to a shortened membrane lifetime. On the other hand, with the Orion electrode, the constant replenishment of the exchanger meant that the process was largely reversible. There was some permanent discolouration of the membrane material though, indicating some irreversible damage, and the electrode had to be recharged after 3 to 4 weeks of intermittent use. This would seem to indicate an accelerated leaching of the sensor material out of the membrane - that this effect was not seen with a CBS electrode may support this inference. In the effluent, the Orion and CBS electrodes yield results which are consistently 20% high. There are two reasons for this occurring. The first reason is that the value of  $\gamma_{Ca^{2+}}$  may have been incorrectly estimated. That is to say, if a value of  $\gamma_{Ca^{2+}}$  resulted from an  $a_{Ca^{2+}}$  reading, then presence of ions which affect the ionic strength but not the electrode

response would increase the ionic strength. Retention of the  $a_{Ca^{2+}}$  value for  $\gamma_{Ca^{2+}}$  would yield a value relatively too high, which would, in turn, give an underestimate of the calcium concentration. However the calcium concentration results are all high, so the estimate of  $\gamma$  is not incorrect due to the change in ionic strength alone. The second way that a 'wrong' value may be determined is if interferent ions are present or if there is some complexation in the sample. The presence of complexation may be ruled out as this would give low results, but the presence of interferent ions would raise the calcium concentration. Thus, any interfering ion will raise the electrode potential, thereby increasing the observed  $a_{Ca^{2+}}$  spuriously. The interferent which shows the most marked effect for all three electrodes is  $NH_4^+$  ion. From Table 5-1 we know that there is ammoniacal nitrogen present in the effluent and some of this may be expected to exist as  $NH_4^+$  at the pH of the samples. It was the presence of  $NH_4^+$  which was suspected to be raising the apparent calcium concentration. The level of  $Mg^{2+}$  was a factor of 20 lower than the  $Ca^{2+}$  and so was unlikely to affect significantly the electrode response - certainly not sufficiently to yield the high results seen.

In the river below the outfall, there was still a large amount of effluent in the sample stream and the same positive bias was observed for the CBS electrode. The Orion electrode was capable of giving a more accurate result in this sample due to its better selectivity.

Notwithstanding the selectivity problem the CBS electrode gave by far the best analytical performance in this type of sample when compared to the other electrodes. The three electrode methods using a CBS electrode gave consistent (but in the presence of large amounts of interferent, high) results and there was no poisoning or shortening in the lifetime of the electrode. The use of a CBS electrode in the river above the effluent gave a reliable measure of the calcium concentration.

#### 5.4 Conclusion.

The use of a CBS electrode for determination of water hardness (Ca + Mg) led to bias due to the small, but definite calcium selectivity of such an electrode.

The application of a CBS electrode to determination of  $\text{Ca}^{2+}$  in a coking oven effluent has shown the advantage of such an electrode in a hostile environment. The intermediate selectivity of a CBS electrode using TAP monomer has shown that careful choice of application must be made. Thus, the level of interferent ions in solution must be such that the CBS electrode can still sense the primary ion accurately. Analysis of a stream water using a CBS electrode and other methods has indicated that such an electrode is capable of giving reliable results. The CBS electrode yielded results comparable with those obtained using an Orion 92-20 and a PVC matrix electrode. Use of electrode techniques in the effluent showed that the Orion and PVC ISE were generally unsuitable for this application as the chemically-hostile sample tended to lead

to rapid deterioration of the membranes. A CBS electrode, whilst unaffected by the degenerating effects of the effluent, yielded high results for calcium analysis due, presumably, to the interfering effect of  $\text{NH}_4^+$  in the solution.

Thus, by reducing the  $\text{Ca}^{2+}$  over  $\text{Mg}^{2+}$  selectivity a robust water hardness electrode might be produced. Whilst an improvement in  $\text{Ca}^{2+}$  over divalent cations and  $\text{NH}_4^+$  selectivity would be capable of yielding a robust Ca ISE. The benefits of having such covalently-bound sensor electrodes would lie in their ability to withstand hostile environmental or chemical plant samples for an extended period. This extended lifetime would be particularly useful for a continuous monitoring application.

CHAPTER 6.

Incorporation of a mediating function.

6.1 From the preceding chapters it will have become evident that useful calcium ISE with covalently-bound sensor groups may be produced. Such electrodes show excellent physical properties and general analytical behaviour. In addition, they may be used in hostile environments which are detrimental to other Ca ISE. However, the limited selectivity of electrodes incorporating triallyl phosphate (TAP), or similar modified phosphate, sensor groups may give rise to limitations in their use. In particular, the divalent cation selectivity might usefully be improved.

Attempts to alter electrode selectivity by modification of the sensor group alone (Chapter 4) were to no real advantage. So, recalling some of the points raised in Chapter 1, one might draw some related conclusions from the previous results of other workers. Specifically, some of the effects attributable to the inclusion of a solvent mediator might be considered in an attempt to see how the performance of a CBS electrode relates to these effects:

- 1) the solvent-mediator dissolves the sensor and allows interaction of the sensor with determinand ions such that a synergistic extraction is effected;
- 2) in a polymeric matrix (e.g. PVC) the degree of plasticisation and, hence, the mobility of species within the membrane is controlled by the quantity of solvent mediator;

- 3) ion-exchange site density is governed by the amount of solvent-mediator, commonly, a 10: 1 excess of solvent-mediator is most effective;
- 4) the solvent-mediator controls the final relative permittivity of the membrane phase.

So, it may be considered whether any of the components of a CBS electrode can give rise to the above effects.

Firstly, in a CBS electrode it is not necessary that the sensor be dissolved as it is covalently-bound. The properties of the polymer or the presence of any unreacted monomer, however, may affect the effectiveness of complexation. In addition, the hydrolysis of a trialkyl phosphate yields a dialkylphosphate and an alkyl alcohol. This alcohol group may be capable of interacting with the ion-site complex. This might result in decreased divalent selectivity in a manner analogous to the effect of decanol on a Ca ISE with a PVC matrix (Table 1-7). It has been suggested that a phosphoryl group is necessary for an effective solvent-mediator effect. This has been frequently shown to be the case (Section 1.3.1.2). As the parent polymer is a hydrocarbon skeleton, then it may be expected to exert little or no effect on selectivity on functional group considerations. Also, only the polymer exists in a 10: 1 ratio to the sensor. Any unreacted monomer or hydrolysis products would exist in much lower quantities and might be expected to exert a proportionately lower effect on selectivity.

Secondly, and perhaps more importantly, the degree of plasticisation of a PVC matrix is very high when used in a calcium ISE. In fact, 60-70% m/m solvent-mediator (e.g. DOPP) is commonly used. This results in a membrane whose properties (both physical and electrochemical) are only slightly removed from those of a liquid ion-exchanger membrane as used in the Orion 92 series electrodes. In this 'solid liquid' the mobility of species within the PVC membrane may be almost as great as within the liquid. This is of considerable importance when recalling the words of Eisenman<sup>45</sup> who suggested that, 'the major restriction when designing ISE for ions other than Group 1a and 1b cations using solid ion exchangers, (e.g. covalently-bound phosphates in CBS electrode) is the tendency for decreases in mobility to offset any increases in ion-exchange affinity for multivalent (or large) cations in solids'. Thus, mobility may not be significantly changed in the PVC matrix, but will be drastically restricted within the 'solid' rubber matrix of the CBS electrode. This reduced mobility may preclude significant divalent selectivity within a CBS membrane.

Finally, only the parent polymer (SBS) exists in sufficient excess (10: 1) to affect the sensor (as discussed above). The relative permittivity,  $\epsilon$ , of the final CBS membrane is controlled by the parent polymer. Choice of an alternative polymer may lead to optimisation of the membrane permittivity but it may not give rise to 'instant selectivity' due to the other factors previously mentioned.

Now, alteration of the sensor has yielded no selectivity advantage to date. So, with regard to the above points, it may be profitable to investigate the incorporation of some kind of mediating function in addition to a sensor. This mediating function may arise from a change in parent polymer or from the incorporation of a material already known to influence selectivity from other researches. A change in polymer would lead to a need for re-optimising membrane parameters. Also, only the relative permittivity, and possibly to a slight extent the sensor site-ion interaction, would be affected using an alternative polymer. So, this approach may be regarded as being of secondary importance. Of primary importance is the incorporation of a solvent-mediator/synergist known to show selectivity enhancement in calcium ISE when used in conjunction with a dialkyl phosphate exchange site.

Such a mediating function might be dioctyl phenylphosphonate or a similar compound with a P=O group which is known to exert a synergistic effect on the extraction of calcium with a dialkyl phosphate exchanger. This mediator may be incorporated into a CBS membrane in either of two ways:

1) Covalent binding.

This approach would be most consistent with the use of a covalently-bound sensor. Both the sensor and mediator groups would be bound to the polymer - so removing the possibility of their loss by leaching. This would be advantageous, as, even with a covalently bound sensor,

loss of mediator has been shown to exert limitations on electrode lifetime<sup>139</sup>. Also, the loss of mediator, by several pathways, has been shown to be an important factor in the lifetime of PVC electrodes<sup>137</sup>. However, the covalent binding of all groups would have its attendant problems. If the mediator were to crosslink the polymer, then the rubber structure would be even further 'tightened' than with a TAP membrane. This may result in, at best, a further reduction in mobility within the membrane. It may also give rise to loss of electrode response due to the formation of an insulating cross-linked membrane. Additionally, steric 'crowding' within the polymer may preclude interaction of the mediator function with the site-cation complex. The use of a monofunctional mediator monomer would not necessarily surmount the problem as such a monomer would show a decreased tendency to polymerise.

2) Entanglement.

This approach has already been used to some effect<sup>138,139</sup> in electrodes utilizing covalently-bound sensors. These studies yielded electrodes with good selectivity but whose lifetime was not extended. An extended electrode lifetime may have been hoped for with a covalently-bound sensor as leaching of the sensor should be eliminated. However, the reason for the short lifetime may have been loss of the mediator<sup>139</sup>. It is this loss of mediator which

would jeopardize the use of this approach in the CBS/TAP system, although some indication of the possibility of selectivity improvement may be obtained. Additionally, problems may arise when using this approach with an SBS membrane. The solvent-mediator will plasticise the SBS membrane and, whilst allowing increased ionic mobility within the membrane, the plasticisers used, e.g. DOPP, may not be compatible with SBS. Also, rubbers do not need plasticisation and, when subject to such modification, may yield membranes with inappropriate mechanical properties. Problems may also be encountered during both the polymerisation and hydrolysis steps of membrane production. In the first instance, the solvent mediator may cause dilution or quenching of the free-radicals so retarding the reaction and resulting in membranes with impaired mechanical and electrochemical properties. In the second instance, the solvent-mediator may be washed out of the membrane or rendered chemically-ineffective by the action of methanolic KOH during the hydrolysis step.

Bearing in mind all the foregoing points, both approaches to mediator incorporation have been used. In the case of a covalently-bound mediator it would be useful to have a model system to act as a co-monomer. Use was made of methyl methacrylate as such a modifying co-monomer as it was easily obtainable and its polymerisation and copolymerisation were well-known. The results

from a study of such a model system would enable the incorporation of a phosphoryl compound to be a much less-empirical process.

## 6.2 Experimental.

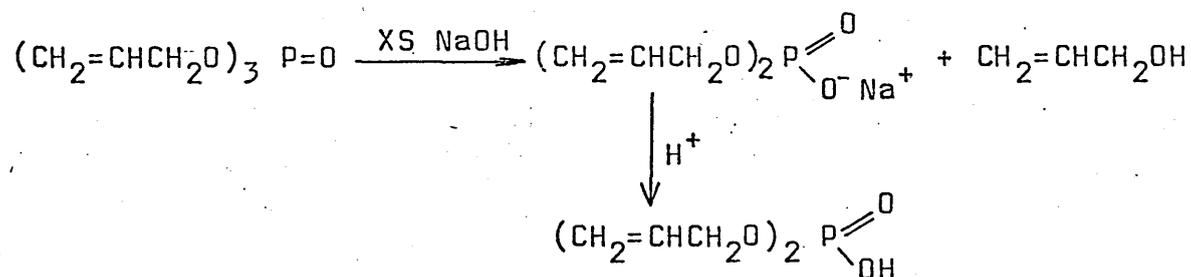
### 6.2.1 Reactants.

#### 6.2.1.1 Triallylphosphate (TAP)

This was treated as previously described (Section 2.3.1.3).

#### 6.2.1.2 Diallyl phosphoric acid (DAPH).

This difunctional monomer was produced by the alkaline hydrolysis of the full ester (TAP). Mild reaction conditions were used in order to prevent formation of the mono-allyl material. The stability of DAPH made further hydrolysis unlikely in any case. The reaction used was analogous to that occurring during hydrolysis of a CBS membrane containing TAP.



Method TAP(20g) was heated at 50 - 60°C for 6 hours with 2M NaOH (100cm<sup>3</sup>) in a 250cm<sup>3</sup> flask equipped with a condenser and a magnetic stirrer. The mixture was left stirring overnight to ensure full reaction. The resulting clear liquid was extracted with diethyl ether (3x50cm<sup>3</sup>), to remove allyl alcohol and any unreacted TAP. The solvent was removed under reduced pressure and the residue checked by IR spectroscopy and weighed to check

the extent of reaction. A further extraction step ( $50\text{cm}^3 \text{Et}_2\text{O}$ ) may be carried out to ensure complete removal of allyl alcohol. The aqueous reaction product was then acidified to pH 1 with 6M hydrochloric acid. This acidification step should take about 2 hours and the solution should be stirred vigorously to ensure complete conversion of the sodium salt to the free acid. Extraction of the aqueous acid with diethyl ether ( $3 \times 50\text{cm}^3$ ,  $2 \times 25\text{cm}^3$ ), (using brine to suppress emulsion formation), drying and solvent evaporation, yielded a clear, very pale straw-coloured liquid which was the free acid. Further purification was accomplished by generation of the calcium salt of the acid<sup>175</sup>. Filtration, drying and reconversion to the acid, followed by extraction into diethyl ether, drying and evaporation of the solvent yielded an almost-colourless clear liquid which yielded the following analytical results:

Infra-red (IR) spectroscopy.

liquid,  $\text{cm}^{-1}$  : 3100 w(alkene); 2960, 2880( $\text{CH}_2$ , aliphatic); 1650 (C=C complicated by P-OH band); 1470(C-H def., aliphatic); 1430 (C-H def., alkene). In addition, the presence of the five characteristic bands<sup>176</sup> may be clearly seen:

$\text{cm}^{-1}$  : 2620, 2320, 1680, 1030(P-O) and\* 510

In addition, the P=O str.band is seen at  $1225 \text{cm}^{-1}$ .

\* KBr plates required to see this band.

## <sup>1</sup>H nmr spectroscopy.

The spectrum consisted of a downfield singlet and the complex (allylic) multiplet.

$\text{CDCl}_3$ ,  $\delta$  (ppm) : 4.4-4.7(q, 4H) ( $-\text{CH}_2-\text{O}-$ ); 5.1-6.4(m, 6H)

( $\text{CH}_2 = \text{CH}-$ ); 9.22(s, 1H) (P-OH).

Ratio of allylic : acid protons = 9.9 : 1.1

On shaking the sample with  $\text{D}_2\text{O}$ , the singlet @  $\delta = 9.22$  ppm disappeared completely leaving the rest of the spectrum as it was previously.

## Mass spectrum.

m/e : 178( $\text{M}^+$ ), 137( $\text{M}^+ - 41$ ) (fragment lost;  $\text{CH}_2 = \text{CHCH}_2-$ )

## Thin layer chromatography.

Single spot,  $R_f = 0.39$  EtOH/1% Acetic acid.

Hazards: Triallyl phosphate is a cancer suspect agent.

Allyl alcohol is a toxic lachrymator.

### 6.2.1.3 Diallyl phenylphosphonate.

The material whose preparation and purification were described in Section 4.2.3 was used.

### 6.2.1.4 Diethylphenylphosphonate (DOPP).

The clear, colourless liquid was obtained commercially (Alfred Bader Collection, Cat.No. S-57593-3, Aldrich Chem.Co.Ltd., Gillingham, Dorset). It was used without further purification.

### 6.2.1.5 Methyl methacrylate.

The commercially-obtained material (Fisons, Loughborough), was distilled under reduced pressure before use. This material

could be stored at 4°C in the dark for period up to 6 months without stabilisation.

#### 6.2.1.6 Polymerisation and Hydrolysis.

Solvent casting from THF solution, as previously described (Section 2.3.2 ), was used throughout. Comonomers and plasticisers were incorporated before pouring into the casting ring. Hydrolysis (where applicable) was accomplished using 5% methanolic KOH.

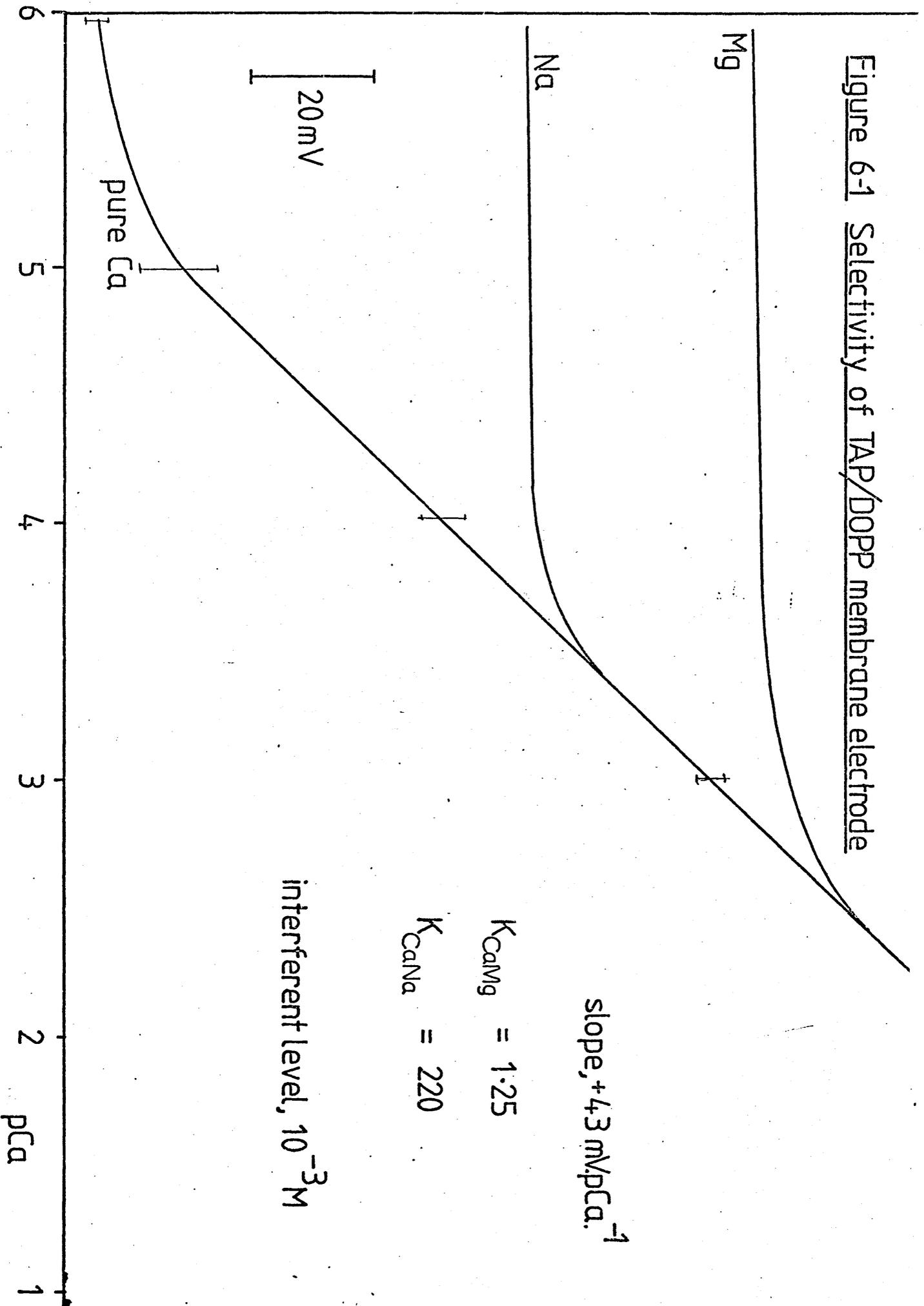
### 6.3 Results and Discussion.

#### 6.3.1 Initial experiences.

By far the most obvious way of incorporating some mediating capacity into a covalently-bound sensor (CBS) membrane was to merely add dioctyl phenylphosphonate (DOPP). This action may have been expected to yield the simplest approach to a more-selective CBS electrode and was, therefore, tried. Some complication was immediately encountered with the question of how and when to incorporate this mediator. There were two answers; during casting; and after hydrolysis, both of which had their merits and disadvantages. The first approach rendered homogeneous incorporation of DOPP simple but, at the same time, made loss on hydrolysis equally facile. In the second approach, loss on hydrolysis was obviated whilst homogeneous mixing may have been difficult, if not impossible.

A membrane was prepared by mixing 10% m/m DOPP with SBS, ABIN and 5.5% m/m TAP and solvent casting from THF solution. The resulting membrane was clear and almost colourless indicating that the presence of DOPP had not adversely affected the

Figure 6-1 Selectivity of TAP/DOPP membrane electrode



polymerisation reaction. Mechanically, the membrane retained elasticity without showing a weakening of the structure. Upon hydrolysis in 5% methanolic KOH for 3 to 5 hours the membrane became slightly yellow and less elastic. Electrodes fabricated from such a membrane tended to be rather difficult to stick to PVC tubing and exhibited  $\text{Ca}^{2+}$  calibration curves with slopes of around  $+ 15 \text{ mV.pCa}^{-1}$ . The use of a shorter hydrolysis time (30 mins., cold 5% KOH/MeOH) yielded, however, an electrode with a larger slope. The performance of this electrode was rather poor (Figure 6-1) showing a significantly hyper-Nernstian slope and poor selectivity. In general, the membrane was difficult to mount and its response was very poor. A large amount of electrostatic noise yielded an imprecise calibration which did not lend this electrode to extensive study. The results obtained, however, indicated that alongside the difficulties of membrane handling, there was no benefit in terms of selectivity. If anything, selectivity was poorer than seen with a TAP electrode. The necessity for mild or short hydrolysis suggested that perhaps the TAP/DOPP membrane was subject to excessive hydrolytic degeneration. This was probably enhanced by the incorporation of DOPP during the casting stage followed by DOPP being leached out during hydrolysis in methanolic KOH—in which DOPP is soluble.

So, the incorporation of DOPP at the casting stage gave rise to difficulties which were not compensated for by any selectivity gains. An attempt was, therefore, made to incorporate DOPP into a TAP membrane after hydrolysis. This approach would

remove the possibility of the leaching out of DOPP during treatment with KOH in methanol. Thus, one working TAP electrode was left to stand in a little DOPP and another inverted and DOPP dropped onto the sensing surface. Neither of these approaches yielded useful electrodes as, after treatment with DOPP, the electrode responses became erratic. The use of DOPP in this manner seemed merely to destroy the surface properties of the working electrodes and yielded no information upon selectivity changes.

Thus, the direct incorporation of DOPP by these techniques was simple, but of little practical value. In the first case, DOPP was being washed out of the membrane during hydrolysis and in the second case, a non-homogeneous DOPP distribution was produced. In the latter case, the production of non-functional and erratic electrode responses indicated the importance of the electrode membrane surface. Thus, it would seem to be necessary to incorporate the solvent mediator during the casting process in order to generate a homogeneous membrane. However, the removal of the hydrolysis step would seem necessary in order to retain the physical and chemical effectiveness of the mediator.

### 6.3.2 Elimination of the hydrolysis step.

One approach circumventing the problems of hydrolysis would be to incorporate diallylphosphoric acid, or even its calcium salt, directly into an SBS membrane. The use of the calcium salt in a polymerisation was discounted on the grounds

that solubility and ability to polymerise were poor. The acid, however, could be simply synthesised and might be expected to polymerise as easily as, say, DAPP. The copolymerisation of the acid (a difunctional monomer) as opposed to TAP (a trifunctional monomer) may lead to some problems. The overall effect in the final membrane would be similar, providing that the  $\text{Ca}^{2+}$  salt could be generated in situ in the polymer membrane. In addition to enabling the incorporation of entangled mediators, the use of diallyl phosphoric acid (DAPH) would generate a covalently-bound dialkyl phosphate sensor without the production of an alcohol fragment in the polymer.

Diallyl phosphoric acid (DAPH) was synthesised and purified (Section 6.2.1.2) and incorporated into an SBS membrane using ABIN initiator and solvent casting from THF solution. The comparative synthetic pathways for production of TAP and DAPH - containing SBS membranes are shown in Figure 6-2. Both routes result in the ultimate formation of a covalently-bound ion-exchanger in the calcium form, but the TAP pathway involves hydrolysis followed by conversion of a  $\text{K}^+$  salt to the  $\text{Ca}^{2+}$  form required. For DAPH there is no hydrolysis step, but the conditioning step may be as important for this system as was the hydrolysis step for TAP electrodes (Chapter 3).

Membranes produced using 5% DAPH lacked the excellent clarity of TAP membranes. These membranes also showed some faint opacity and tended to be slightly yellow and less elastic than

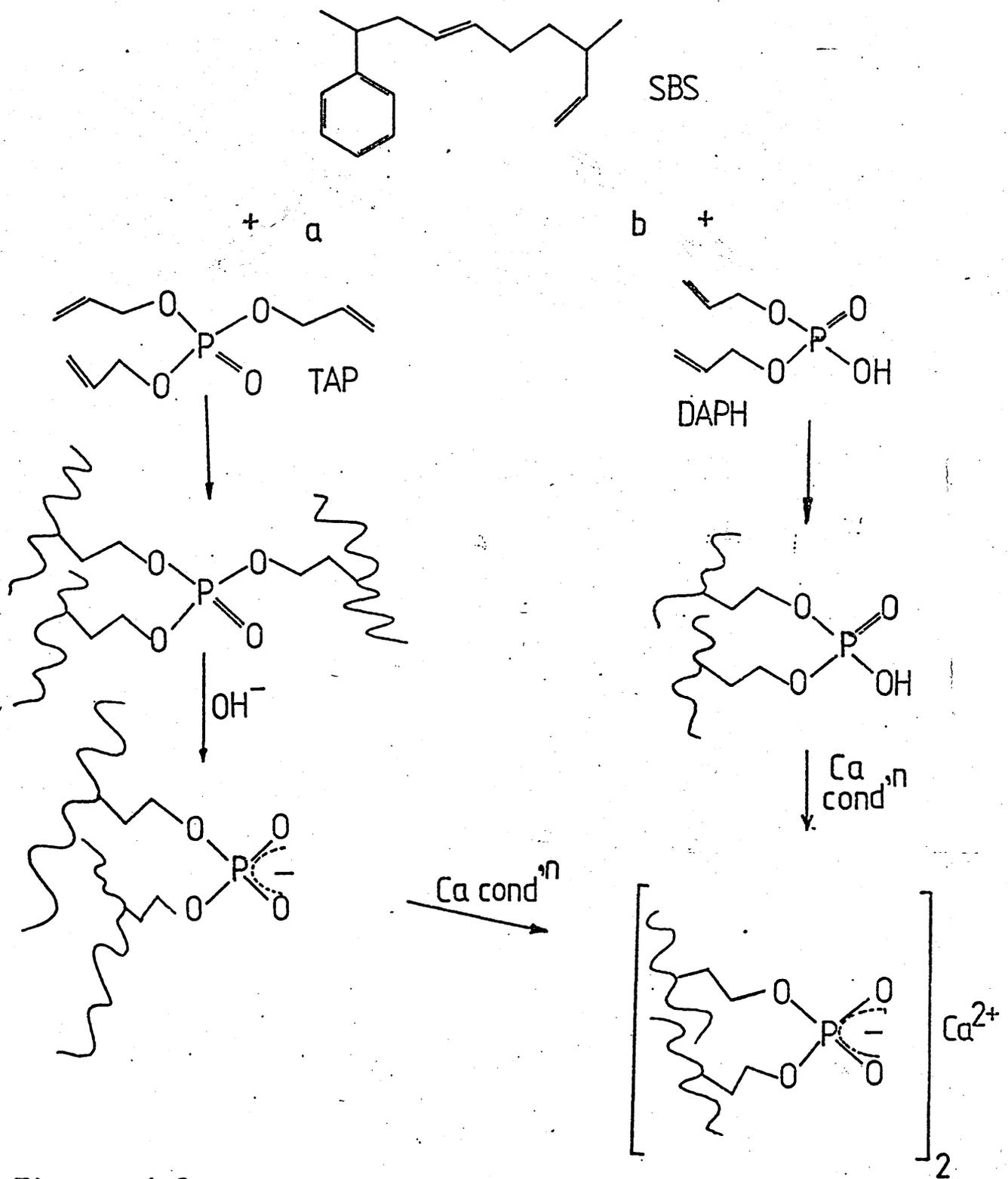


Figure 6-2

Two approaches to the production of a covalently-bound dialkylphosphate Ca sensor.

their TAP counterparts. Despite the opacity, DAPH membranes were crosslinked - as indicated by their insolubility in THF. On soaking in aqueous solution, the membranes became less brittle and took on the pale yellow coloration seen with hydrolysed and conditioned TAP membranes. Due to the slight brittleness of a DAPH membrane, discs of the material were cut out after soaking the membrane in warm water or methanol for a few minutes. Any cracks which were formed in the active membrane were found to give rise to an anionic electrode response as had been noted for other 'crack' electrodes. Such electrodes could be diagnosed by their low d.c. resistance ( $<10^6 \Omega$ ) or by close inspection under an optical microscope.

The electrochemical responses of two electrodes made from a membrane containing 5% DAPH and conditioned in a solution of  $10^{-3} \text{M Ca}^{2+}$  and  $10^{-3} \text{M H}^+$  are shown in Figures 6-3 and 6-4. The calibration slopes of both electrodes was excellent, showing slopes very closely approaching the 'ideal' Nernstian value ( $29.6 \text{ mV.pCa}^{-1}$ ). Linear response ranges were at least as good as seen with TAP electrodes, showing limits of detection in the region of  $2 \times 10^{-6} \text{M Ca}^{2+}$ . As was the case with TAP electrodes, and contrary to the behaviour of PVC electrodes, this lod was not limited by the sensor leaching from the membrane and dissociating in the test solution. In addition to the Nernstian calibration slope and a favourable lod, these electrodes showed excellent run-to-run precision and had lifetimes in excess of one month. However, the selectivity was poorer than that seen with TAP electrodes, particularly in the presence of  $\text{Na}^+$  ions.

Figure 6-3 Selectivity plots for 5% DAPH membrane electrode

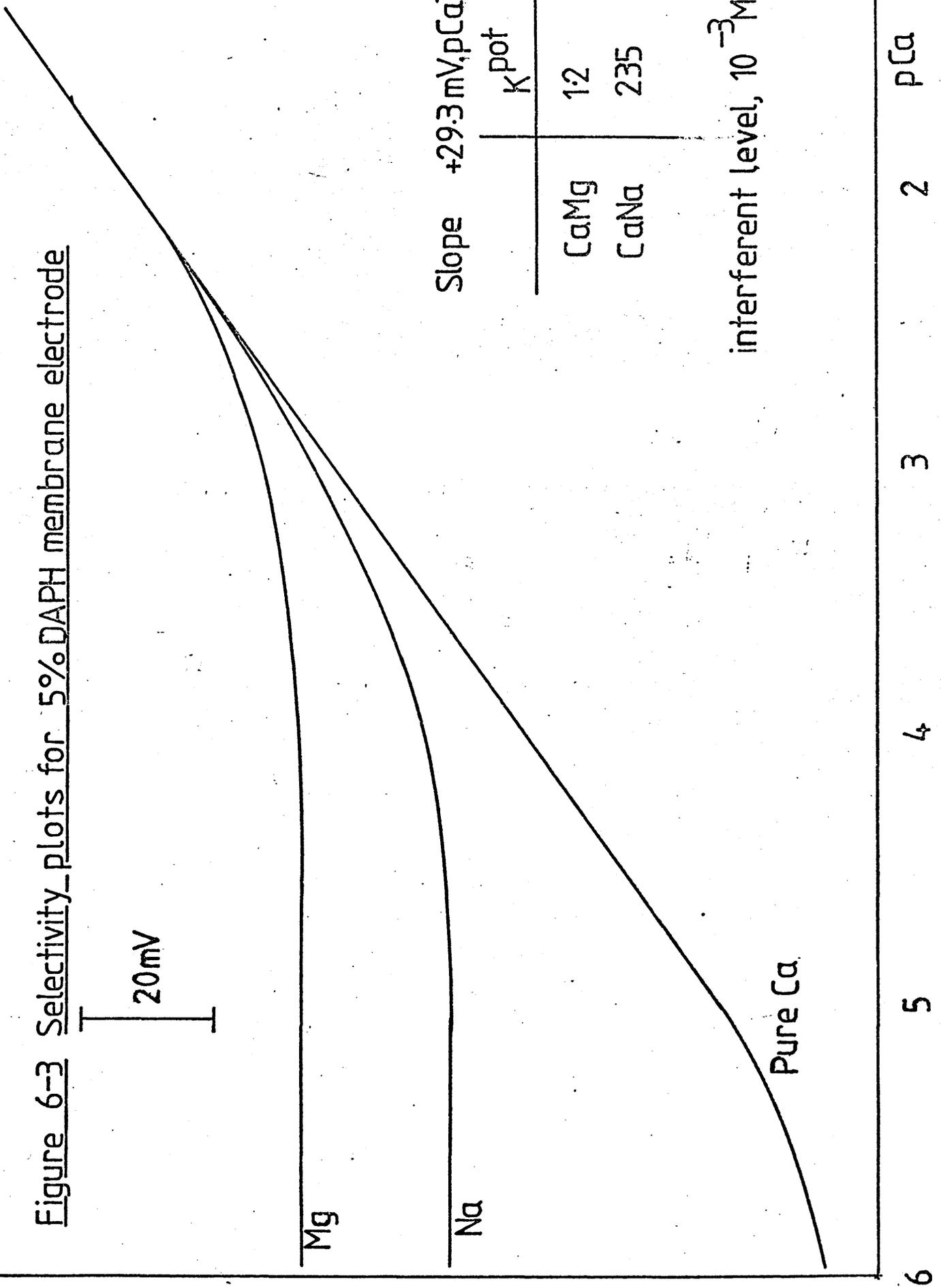
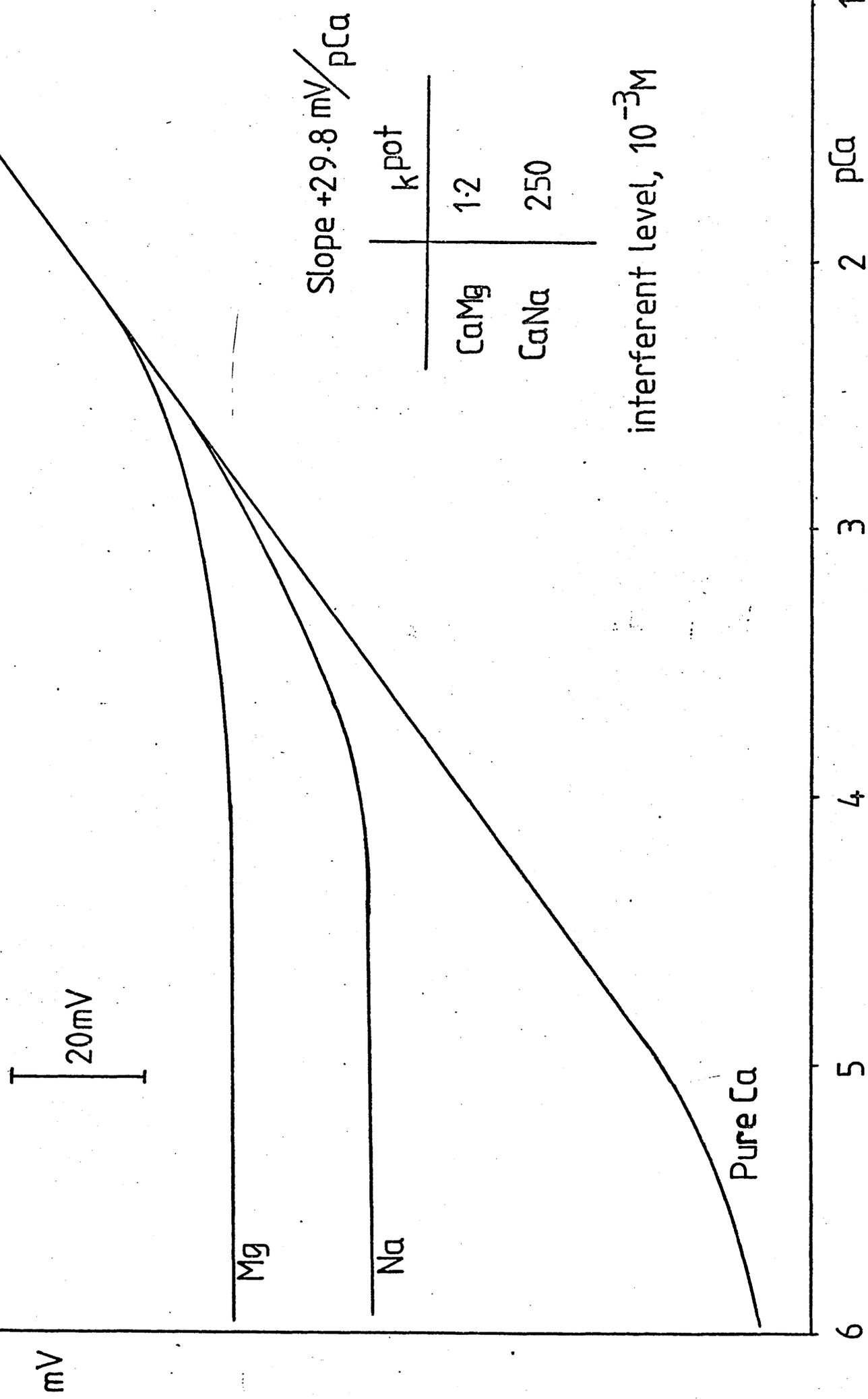


Figure 6-4 Selectivity plots for 5% DAPH membrane electrode

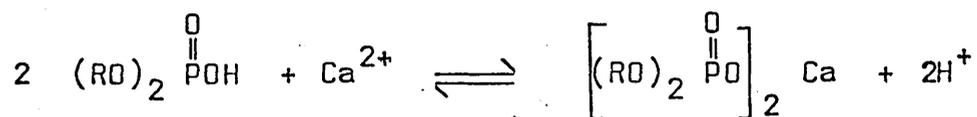


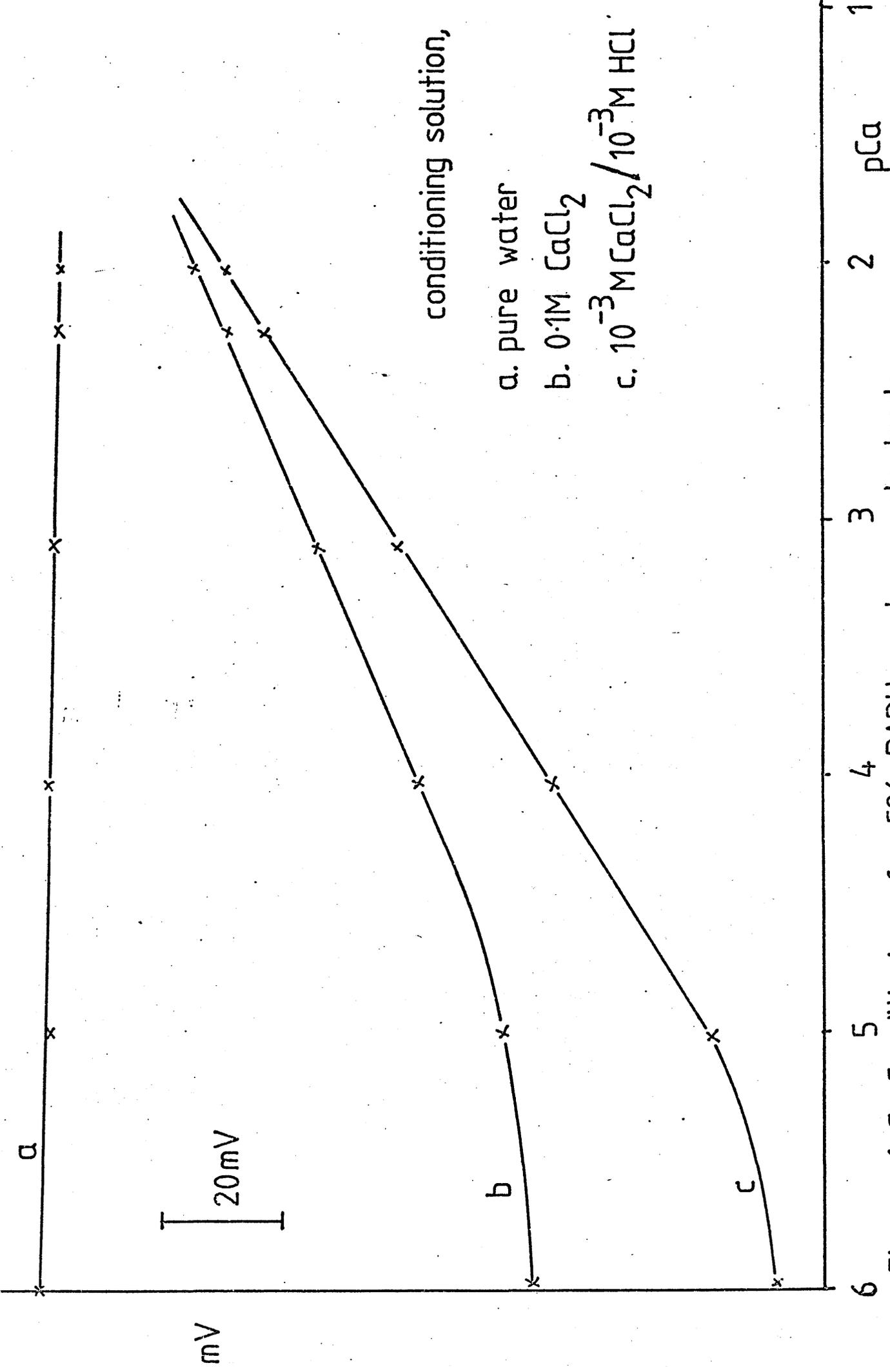
This decreased selectivity may have been the result of different polymer morphology induced by DAPH monomer which was apparent from the lack of elasticity seen with DAPH membranes. Moreover the DAPH membranes had not been hydrolysed. However, this removal of the hydrolysis step might have been expected to improve  $\text{Ca}^{2+}$  over  $\text{Mg}^{2+}$  selectivity as there would be no generation of an ROH function in the polymer when using the DAPH route. This improvement in selectivity over  $\text{Mg}^{2+}$  was clearly not seen. Other than differing physical characteristics, there may be other underlying factors emphasising the difference between membranes made using TAP or DAPH monomer.

During hydrolysis of a TAP membrane in methanolic KOH, the polymer structure is 'opened up' by some swelling of the membrane in the solvent. This swelling enables generation of the  $\text{K}^+$  form of the exchanger right through the membrane and subsequent conditioning in  $\text{Ca}^{2+}$  of the open-structured polymer allows exchange of these sites. When there is no hydrolysis (with DAPH membranes) the polymer structure may stay more tightly closed and reduce the ability of  $\text{Ca}^{2+}$  ions to enter the bulk membrane. The smaller, more mobile  $\text{Na}^+$  ion may be capable of entering the membrane more easily - so causing poorer  $\text{Ca}^{2+}/\text{Na}^+$  selectivity. The poorer  $\text{M}^{2+}$  (over  $\text{M}^+$ ) selectivity of the DAPH electrodes may be a consequent of more than one factor. In addition to the above factors, the production of DAPH membranes has not been as extensively optimised as the TAP system.

The occupation of ion-exchange sites would appear to be important, as is, obviously, the type of ion exchange site generated. It was noticeable that the slope of the calcium calibration curve for a DAPH membrane electrode was affected by the conditioning process. This was to have been expected as slope is dependent upon ion-exchange site density. Thus, three electrodes made from a membrane which contained 5% DAPH were conditioned in three different media (Figure 6-5). Conditioning for 3 days in deionised-distilled water yielded an electrode which did not respond to  $\text{Ca}^{2+}$  ions. Conditioning in 0.1M  $\text{CaCl}_2$  yielded an electrode showing a slope of  $+18 \text{ mV.pCa}^{-1}$  and an lod of  $10^{-5}$  whilst conditioning in a solution containing  $10^{-3} \text{ M CaCl}_2$  and  $10^{-3} \text{ M HCl}$  yielded an electrode with a slope of  $+26 \text{ mV.pCa}^{-1}$  and an lod of  $2 \times 10^{-6} \text{ M}$ . Thus, it seemed essential that a certain activity of cations be present during the conditioning of DAPH membranes if functional electrodes were to result. This may have implications in later discussions of the mechanism of response. The advantageous performance of acid-conditioned electrodes does, however, raise various points.

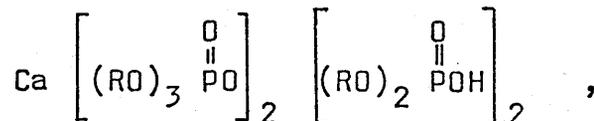
In terms of ion-exchange site generation, the strong (0.1M) calcium solution might have been expected to have generated more ion-exchange sites in the calcium form by pushing the equilibrium (below) to the right hand side.



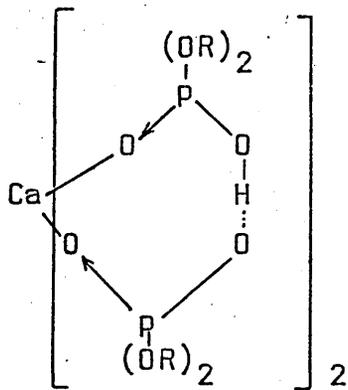


6 Figure 6-5 Conditioning of a 5% DAPH membrane electrode

However, the difficulty of generating the  $\left[ (\text{RO})_2 \overset{\text{O}}{\parallel} \text{PO} \right]_2 \text{Ca}$  species may tend to work against this. In mixed  $\text{Ca}^{2+}/\text{H}^+$  conditioning, the presence of  $\text{H}^+$  will drive the above equilibrium to the LHS. More importantly, the use of a mixed conditioning solution may generate a different ion exchange site. For instance, Griffiths<sup>132</sup> found that a PVC matrix calcium ISE containing the mixed salt;



yielded superior performance to electrodes based upon either  $\text{Ca} \left[ (\text{RO})_2 \overset{\text{O}}{\parallel} \text{PO} \right]_2$  or  $(\text{RO})_2 \overset{\text{O}}{\parallel} \text{POH}$  alone. The reasons for this were thought to lie in the availability of alternative ion-exchange sites for calcium. However, the formation of the hydrogen-bonded, mixed complex;



which has been suggested<sup>96</sup> to be present in the extraction of cations by dialkylphosphates, may also have been important. In the case of DAPH membranes, both effects may also have had some influence. So,  $\text{Ca}^{2+} - \text{H}^+$  exchange may have been occurring

or the mixed chelate may have been formed, so enhancing the electrode slope after conditioning in a mixed  $\text{Ca}^{2+}/\text{H}^+$  solution. The presence of  $\text{Ca}^{2+}/\text{H}^+$  exchange may have been the more dominant factor as the steric requirements for the above 4-coordinate chelate may not have been met when the ligating groups were bound into a polymer matrix.

Whatever the reason, or combination of reasons, responsible for the observed selectivity and response changes, such behaviour puts a DAPH electrode at a disadvantage. That is to say, any mediating function used in a DAPH electrode will have to exert a comparatively greater influence on selectivity than would be required with an electrode showing the selectivity of TAP membranes. In fact, having dispensed with the hydrolysis step in membrane fabrication by the use of DAPH, the use of a mediating function becomes more desirable due to the poorer selectivity of the resulting electrode.

### 6.3.3 Covalently-bound mediators.

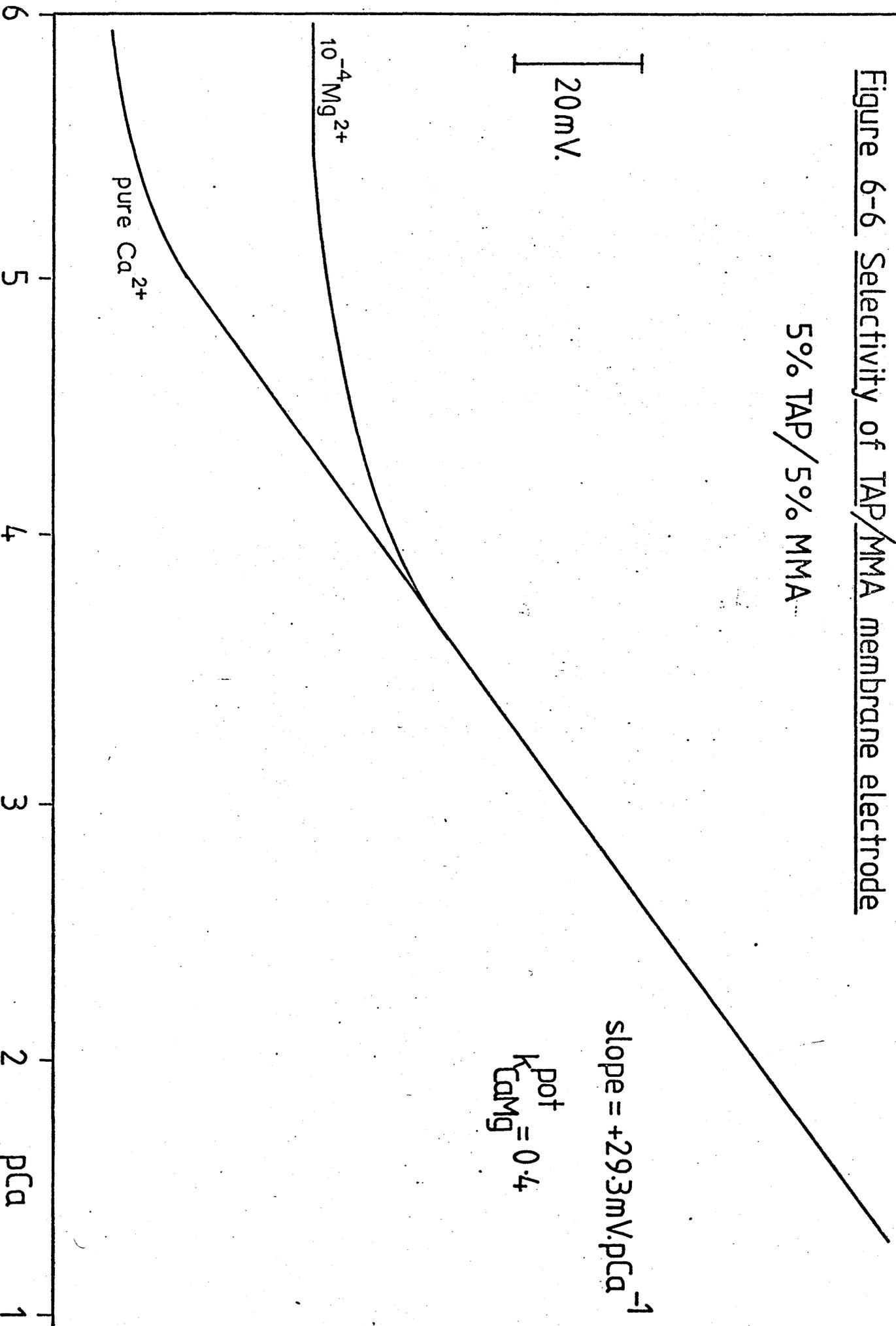
As no selectivity advantage had been gained from the use of a membrane containing TAP and entangled DOPP, the incorporation of a covalently-bound mediating function was investigated. Although hydrolysis had been found to remove or modify the entangled mediator, a covalently-bound mediator could not be detached from the polymer. It could, however, be chemically modified. It would be necessary to incorporate the mediator homogeneously into the membrane. In addition, it would

be useful if all the reactants could be intermixed and the polymerisation all carried out by the same method. For these reasons, a model system was chosen, which would yield information so that, hopefully, a functional mediator could be incorporated into the SBS/TAP system. Methyl methacrylate (MMA) was chosen as a model co-monomer due to its ready availability, ease of purification and degree of polymerisability.

Membranes were produced using SBS, 5% m/m TAP and either 5 or 10% m/m methyl methacrylate (MMA) by solvent casting from THF solution and using ABIN/u.v. initiation. Reactants were mixed together before being poured into the casting apparatus. The resulting polymer films were homogeneous and, therefore, clear, but had a slight yellow tinge and were quite brittle. The membrane containing 10% MMA was extremely brittle and great care had to be exercised in taking disc samples for mounting into electrodes. Softening of this membrane in warm water or methanol before cutting was mandatory for the production of membranes with no cracks. As would be expected, the use of membranes containing micro-cracks yielded electrodes showing an anionic response, so inspection of mounted discs using a microscope was essential. Hydrolysis of these TAP/MMA membranes had to be carried out under mild conditions (30 mins., cold 5% methanolic KOH), as strong or extended hydrolysis tended to result in brown membranes with a narrow linear pCa range. The effect of hydrolysis was to generate the dialkylphosphate sensor and a carboxylate anion (from the methacrylate moiety).

Figure 6-6 Selectivity of TAP/MMA membrane electrode

5% TAP/5% MMA



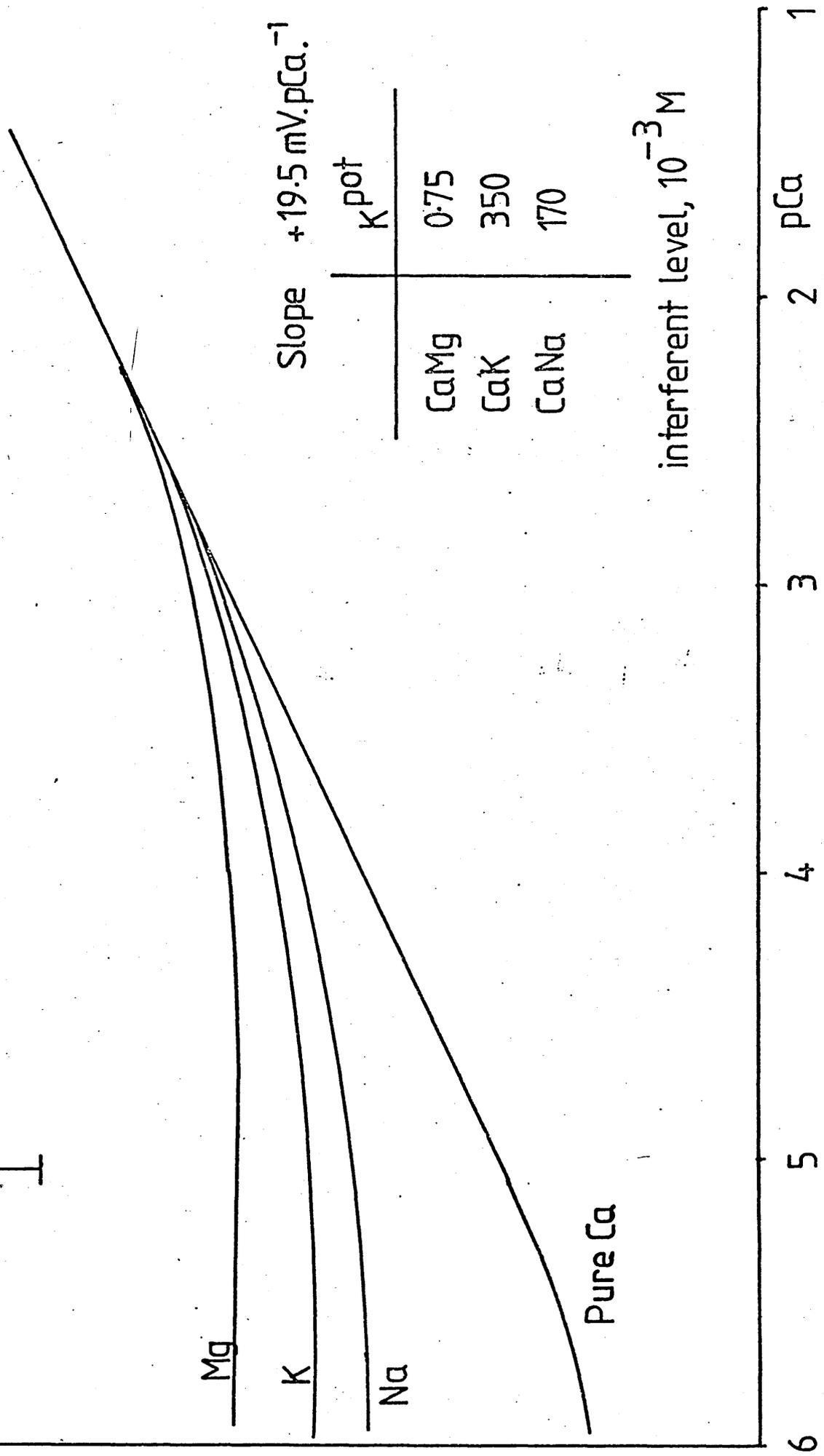
An electrode made from a membrane containing 5% m/m MMA (Figure 6-6) showed a  $\text{Ca}^{2+}$  calibration slope of  $+29.3 \text{ mV.pCa}^{-1}$ . In the presence of a background level of  $10^{-4} \text{ M Mg}^{2+}$  interferent, a selectivity coefficient,  $k_{\text{CaMg}}^{\text{pot}} = 0.4$  was obtained. This indicated little or no effect on  $\text{Ca}^{2+}/\text{Mg}^{2+}$  selectivity when compared to TAP, as might have been expected from a system in which no P=O synergist was present. The lod of this electrode was  $4 \times 10^{-6} \text{ M Ca}^{2+}$  and the general analytical performance of the TAP/MMA electrode was poorer than for a membrane containing TAP alone. In particular, the higher resistance ( $\sim 10^8 \Omega$ ) of such electrodes gave rise to noisy responses and the lifetimes of these TAP/MMA electrodes was limited to around 1 month by their increasing brittleness.

A membrane containing 10% MMA was also produced in order to investigate how much of a co-monomer could be introduced into an SBS/TAP membrane before severe electrochemical and physical limitations arose. Such a membrane was clear and slightly yellow, and, as for the 5% MMA analogue, was subject to rapid hydrolytic degradation. In addition, the membrane was extremely brittle due to the large amount of copolymerised MMA and the electrodes resulting from this membrane showed high resistances which gave rise to noisy responses. Electrodes with such a high level of MMA showed  $\text{Ca}^{2+}$  calibration slopes which did not exceed  $+20 \text{ mV.pCa}^{-1}$  but whose selectivity over  $\text{Mg}^{2+}$  was not much worse (Figure 6-7) than for TAP electrodes. Selectivity over monovalent cations was poorer, however, and this may have been due to the ability of the

Figure 6-7 4.5% TAP/ 91% MMA membrane — selectivity\_ plots

V

20mV



Mg

K

Na

Pure Ca

6

5

4

3

2

pCa

1

carboxylate group to exchange  $\text{Na}^+$  and  $\text{K}^+$ . The general analytical performance of these electrodes was poor. High resistances ( $10^8 - 10^9 \Omega$ ) resulted in very erratic, electrostatically-affected responses and run to run drift could only be minimised by extensively washing the membrane.

Although electrodes incorporating MMA did not yield more-selective calcium electrodes, this was neither planned or to be expected. What these studies did indicate, however, was that a simple co-monomer could be incorporated into the SBS/TAP model system. A high level of co-monomer incorporation was found not to be advantageous, though, and indicated that obtaining the recommended 10: 1 mediator:sensor excess, when using a covalently-bound mediating function, may prove difficult.

After the successful use of the model MMA system, a covalently-bound phosphonate was incorporated into a membrane. The phosphonate chosen was diallylphenylphosphonate (DAPP) as this had already been synthesised and shown to copolymerise readily, (Sections 4.2.3 and 4.3.3). In order to preserve the dialkylphosphonate as a mediator, the hydrolysis step would have to be by-passed by use of DAPP sensor. Such a phosphonate mediator in conjunction with a dialkylphosphate sensor might be expected to influence electrode selectivity for  $\text{Ca}^{2+}$  over  $\text{M}^{2+}$  in much the same way that DOPP does in PVC electrodes. The experiences from using MMA as comonomer suggested that high levels of co-monomer were not beneficial. This, of course, precludes a 10: 1

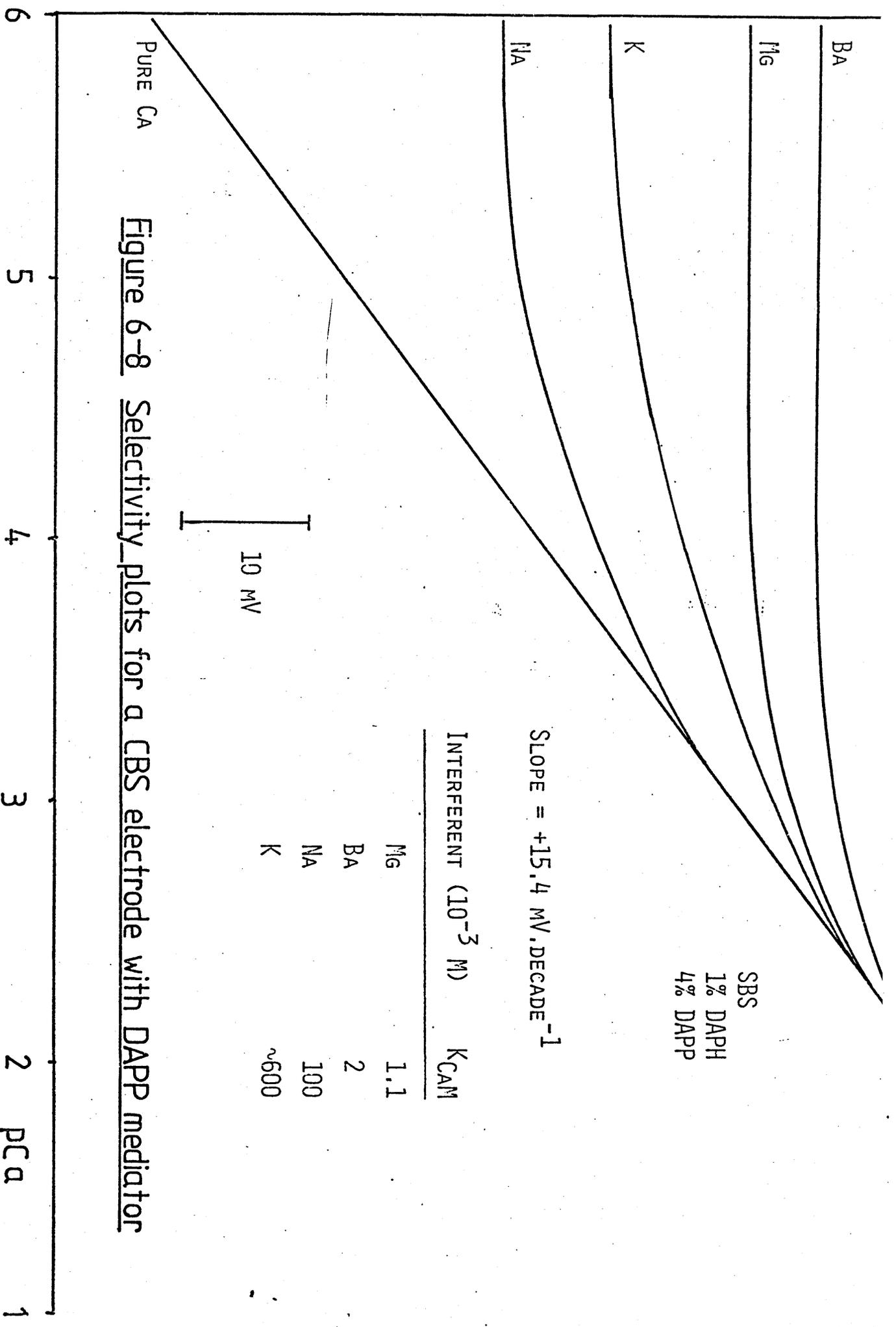


Figure 6-8 Selectivity plots for a CBS electrode with DAPP mediator

mediator ratio usually. So, a membrane was prepared in which the total quantity of monomer and co-monomer (DAPH + DAPP) was maintained at 5% m/m. Thus, 1% DAPH and 4% DAPP were used which gave a mediator-sensor ratio of 4: 1. When copolymerised with SBS, a clear, colourless membrane was produced. Sections of this membrane were mounted into electrode bodies and conditioned in mixed  $\text{Ca}^{2+}/\text{H}^+$  ( $10^{-3}\text{M}$ ) solution. Electrode calibration slopes for such a membrane seldom exceeded  $+18\text{mV.pCa}^{-1}$ , irrespective of the membrane orientation and often showed a poor pCa range. Despite this, the response of one such DAPH/DAPP electrode was sufficiently stable to obtain selectivity plots (Figure 6-8) which indicated a slight worsening of selectivity for  $\text{Ba}^{2+}$  and  $\text{K}^+$  when compared to a membrane containing 5% DAPH alone. The reason for the consistently low electrode calibration slopes was thought to lie in the low level of sensor (1% DAPH) used in this membrane. This may have been further supported by the fact that many of these electrodes showed a 'tailing off' of calcium response at high  $a_{\text{Ca}^{2+}}$  (Figure 6-9). Thus, a 1% level of sensor might have yielded insufficient ion-exchange sites to allow exchange in higher  $a_{\text{Ca}^{2+}}$  solutions. Consequently, there was little or no ion-exchange (and, therefore, membrane potential) at the outer membrane/test-solution interface and all solutions of calcium activity greater than  $10^{-3}\text{M Ca}^{2+}$  yielded essentially the same potential. This study indicated then, the need to incorporate more than 1% sensor in order to obtain a Nernstian

Figure 6-9 Calibration of a 1%DAPH / 4%DAPP membrane electrode

mV

20mV

slope =  $+24.5\text{mV pCa}^{-1}$

pure Ca

pCa

6

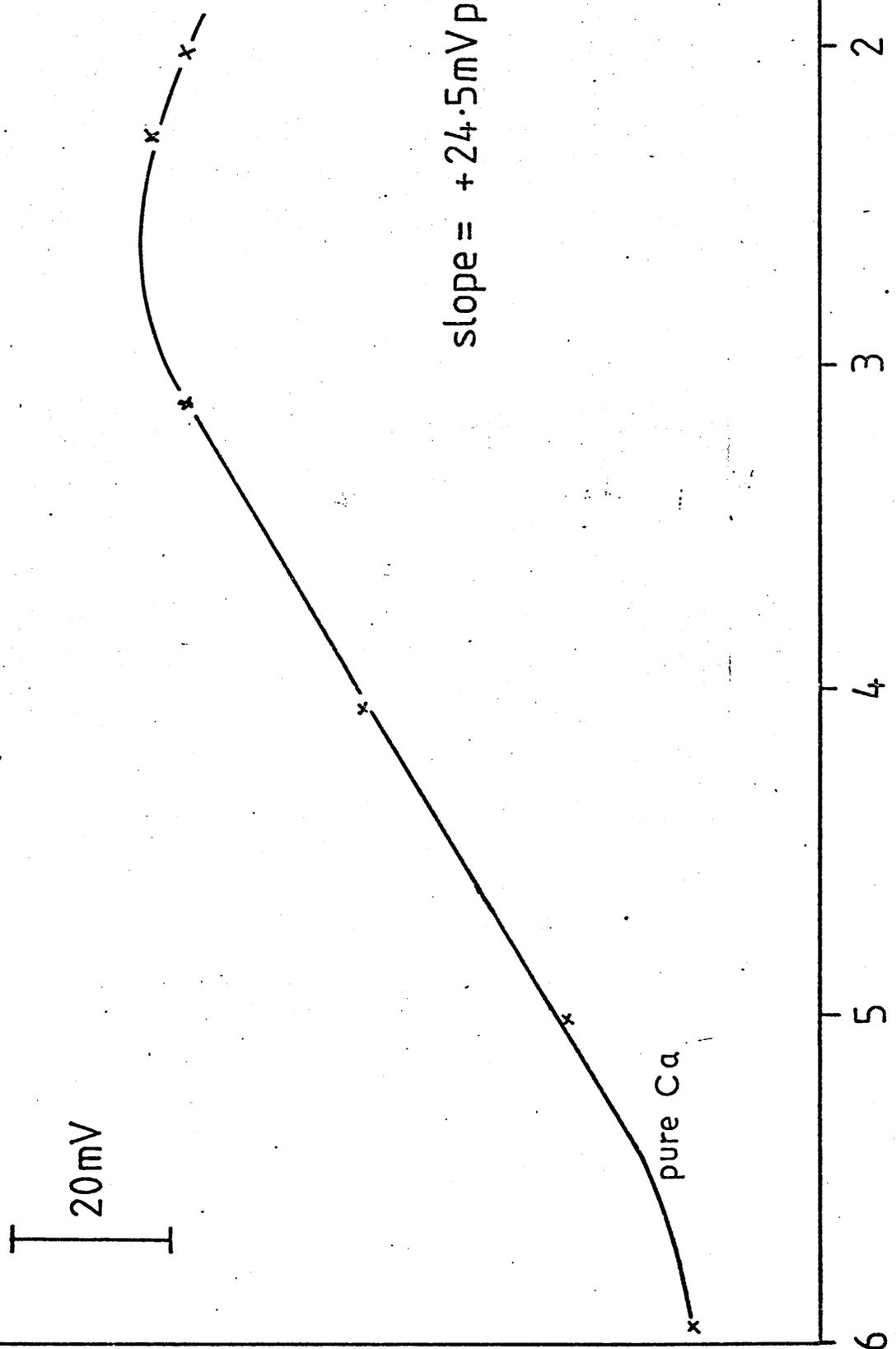
5

4

3

2

1



response over a wide calcium activity range.

The use of 4.5/5% m/m sensor seemed to give the best results, but the incorporation of a covalently-bound mediator when using such a level of sensor posed certain constraints. Firstly, the requirement for excess mediator (commonly a 10-fold excess over sensor) meant that the use of a mediator, such as DAPP, which crosslinked the polymer structure, at such a level, would yield a very highly-crosslinked polymer membrane. This membrane would be likely to exhibit poor mechanical properties, e.g. brittleness, and to have a high resistance. Such a membrane would be unlikely to yield functional electrodes, although the use of a monofunctional, non-crosslinking monomer may reduce the problem. Secondly, even if a mediator could be covalently-bound into the polymer structure at the levels required, there is no guarantee that the mobility of species within the electrode membrane would be sufficient to permit divalent selectivity. Also, even if the sensor-site and mediator were present in the required proportions, their ability to interact with the ion simultaneously may be severely restricted by the 'solid' polymeric matrix. The above possibilities serve to illustrate the highly complex interactions which may occur in covalently-bound sensor membrane ISE. It is for these reasons that the experimental investigation of the various parameters may yield the greatest insight into the membrane function. Thus, investigations of systems containing an entangled mediator were continued concurrently with those using a covalently-bound

mediator. The utility of having both a covalently-bound and an entangled mediator in the same membrane must not be overlooked as such an approach may reap benefits from both systems.

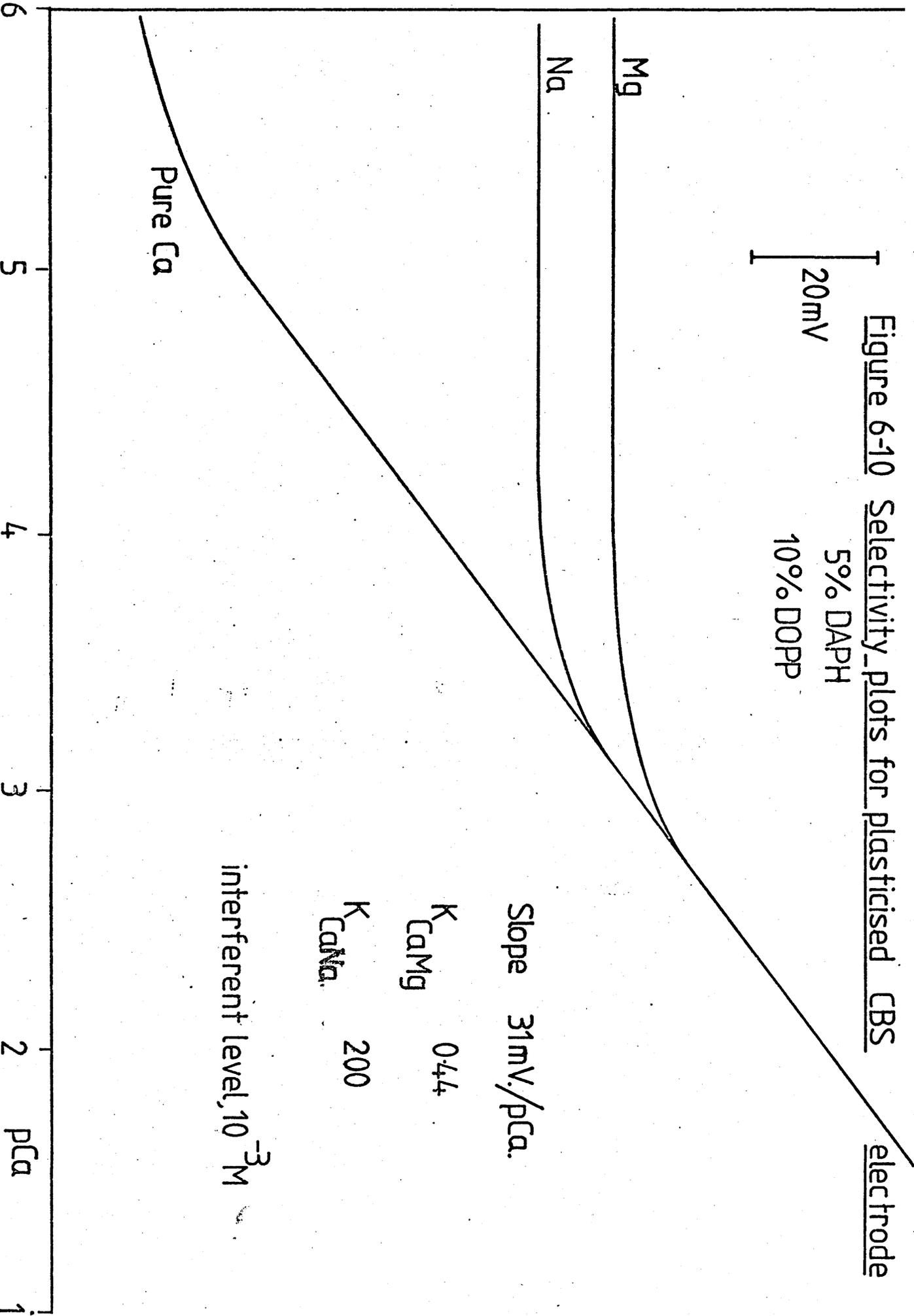
#### 6.3.4 Entangled mediators.

From the studies conducted by other workers into calcium ISE selectivity, it has become obvious that dioctylphenylphosphonate (DOPP) has yielded the most-selective electrodes when used with a dialkylphosphate sensor. As this material was commercially or synthetically available it was used in a CBS electrode. Early results from membranes using TAP and DOPP had suggested that the hydrolysis step was removing DOPP thereby rendering no benefit in selectivity. With the production of DAPH, and its successful use as a covalently-bound sensor in an ISE requiring no hydrolysis, the opportunity arose to combine the benefits of DAPH and DOPP.

With the knowledge that the sensor ought to be kept at the 5% level and that DOPP would plasticise the rubber membrane, a membrane containing 5% DAPH and 10% DOPP was prepared. This membrane was clear and colourless and showed an increased elasticity over a membrane containing DAPH alone. This increased elasticity was, in fact, a benefit and enabled the membrane to be processed more easily. Discs of this membrane were cut out and mounted into an electrode body. Sticking of the plasticised rubber to PVC tubing proved to be difficult and overnight drying of the adhesive was allowed before wetting the sensor unit. Conditioning of such a membrane in mixed  $\text{Ca}^{2+}/\text{H}^{+}$  solution

Figure 6-10 Selectivity plots for plasticised CBS electrode

20mV  
5% DAPH  
10% DOPP



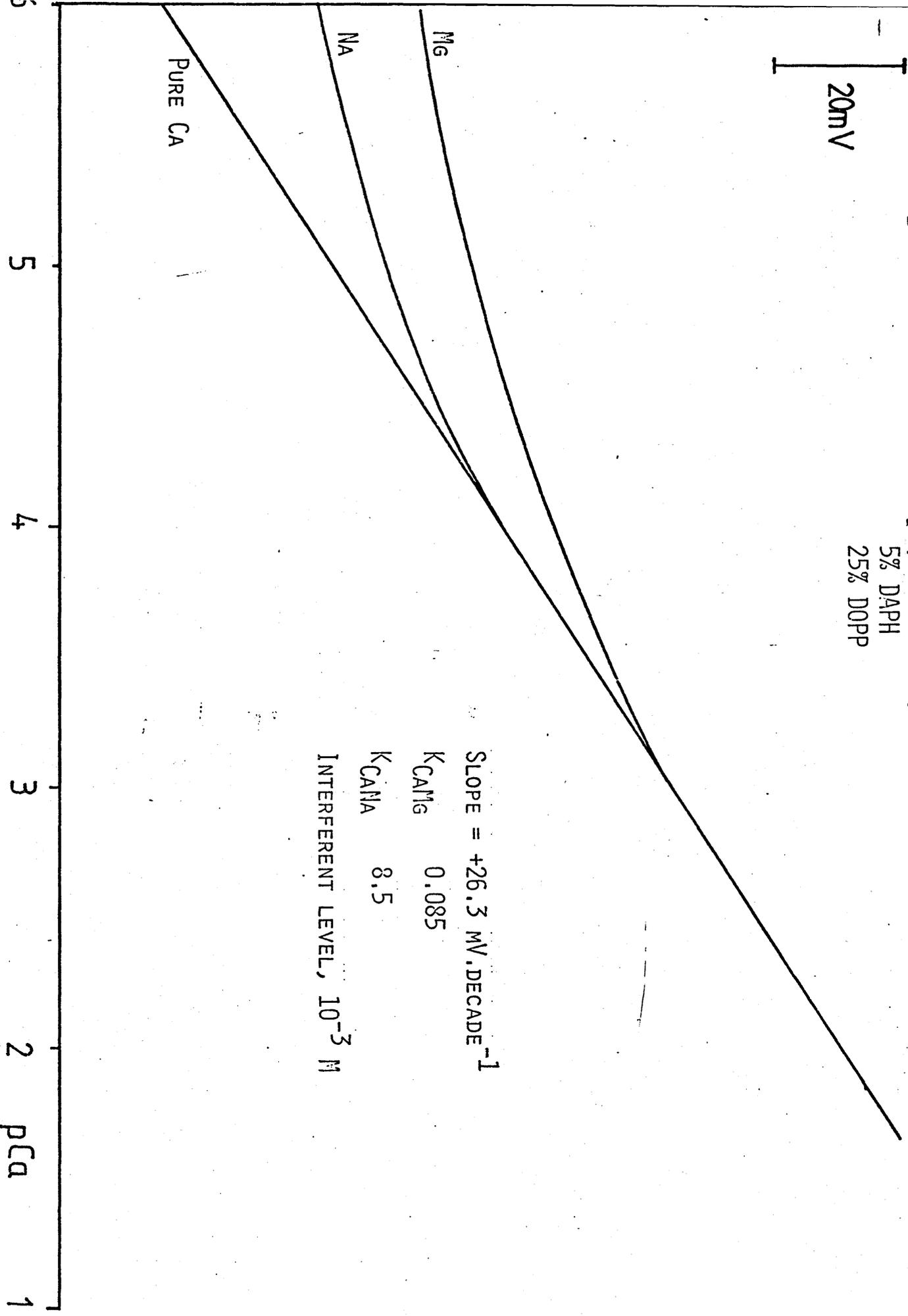
yielded the calcium response and selectivity plots shown in Figure 6-10. The  $\text{Ca}^{2+}$  calibration slope was near-Nernstian with an lod of around  $10^{-6}\text{M Ca}^{2+}$ . Selectivity coefficients,  $k_{\text{CaM}}^{\text{pot}}$  ( $\text{Mg}^{2+} = 0.44$  and  $\text{Na}^{+} = 200$ ) indicated a distinct improvement in selectivity when compared to a membrane containing 5% DAPH alone ( $\text{Mg}^{2+} = 1.2$  and  $\text{Na}^{+} = 250$ ), particularly for  $\text{Mg}^{2+}$ . This performance was maintained for at least one month and general analytical performance was good, showing fast, stable responses. The results from this electrode were promising and as the inclusion of 10% DOPP had made general electrode improvements for DAPH membranes in all respects but for fabrication, the level of DOPP was increased.

So, a membrane containing 5% DAPH and 25% DOPP (a 1: 5 ratio) was prepared. The membrane polymerised to yield a clear, slightly mottled film which was very elastic. Mechanically, the membrane was far weaker and more elastic than one containing 5% DAPH alone, but was not so over-plasticised that it became flaccid as seen with some PVC membranes. Discs which were cut from this membrane were extremely difficult to stick using IS496 adhesive. This was due to the 'oily' surface film on the membrane which became noticeable with the high level of plasticisation. The use of an activator and adhesive was found successful, but careful sealing of the glue-line was necessary to avoid anionic responses in the resulting electrodes. Electrodes were checked for effectiveness of sealing by their d.c. resistance in  $10^{-3}\text{M CaCl}_2$  solution. An electrode whose unconditioned resistance

Figure 6-11 Selectivity plots for plasticised CBS electrode

5% DAPH  
25% DOPP

20mV



was less than or equal to  $10^6 \Omega$  could be safely assumed to have a leak and be discarded. Figure 6-11 shows the response of an electrode which was successfully fabricated from a 25% DOPP membrane. The electrode was conditioned in mixed  $10^{-3} M Ca^{2+}/10^{-3} M H^+$  solution and showed a slightly sub-Nernstian  $Ca^{2+}$  calibration slope with an lod of around  $10^{-6} M$  again.

Selectivity of this electrode was markedly improved, selectivity coefficients,  $k_{CaM}^{pot}$  were much lower than for previously produced membranes as shown below:

Selectivity Membrane	$k_{CaM}^{pot}$		Interferent level
	$Mg^{2+}$	$Na^+$	
TAP	0.3	30	$10^{-3} M$
DAPH	1.2	250	"
DAPH/DOPP(1: 2)	0.44	200	"
DAPH/DOPP(1: 5)	.085	8.5	"
PVC <sup>138</sup>	.086	1.1	$10^{-3}, 10^{-2}$

Selectivity of a 25% DOPP electrode, therefore, was similar to that of a 'state of the art' PVC calcium ISE. This great improvement in selectivity for the CBS electrode was despite the mediator:sensor ratio being only 5: 1 where contemporary Ca electrodes use a 10: 1 ratio. Although the selectivity of such an electrode was very favourable and much-improved, this was not without some disadvantage. Thus, the lifetime of such an electrode was of the order of days as selectivity degenerated to that typical of an electrode membrane containing DAPH alone. This would seem to indicate that the loss of the selectivity-inducing

DOPP was the limiting factor      in agreement with the work of other researchers<sup>137,138,139</sup>. In connection with the shortened effective lifetime of these electrodes, continued blotting of a 25% DOPP membrane tended to result in a worsening of performance and often gave a displacement of the calibration line. This may have been due to the removal of DOPP from the all-important membrane surface layer. However, it was evident that the inclusion of even a 5: 1 mediator:sensor ratio resulted in a dramatic improvement in electrode selectivity, particularly over  $Mg^{2+}$ . This may have arisen from two processes. Firstly, the level of phosphonate capable of giving rise to a synergistic enhancement had been significantly increased such that there was more chance of that synergism occurring. Secondly, the level of plasticisation, and, therefore, the mobility of divalent ions, within the membrane phase had been significantly increased by the inclusion of DOPP. It is likely that both effects were making a significant contribution to the overall enhancement of selectivity.

#### 6.4 Conclusions.

Attempts to improve selectivity in the basic TAP-containing CBS electrode have not only yielded these selectivity improvements but have also provided an insight into the possible working mechanisms of such electrodes.

The use of mediators with TAP membranes led to electrodes whose selectivity was not improved, but which showed that additional monomers could be incorporated alongside TAP.

Such an approach also indicated the desirability of removing the hydrolysis step in membrane production. The preparation of diallyl phosphoric acid and its successful incorporation into an SBS matrix have shown that a covalently-bound diallylphosphate sensor group may be produced by either of two pathways.

Use of the directly-copolymerised diallylphosphate made it possible to incorporate mediating functions into a CBS electrode with no risk of modification during hydrolysis. Incorporation of DAPP as a covalently-bound mediator yielded electrodes showing poor general performance and inadequate selectivity. This was attributed to the low level of sensor and the low mediator:sensor ratio obtainable using that approach.

The incorporation of entangled DOPP as mediator in a DAPH membrane led to the successful production of a membrane electrode with a highly-selective response to calcium over  $Mg^{2+}$  and  $Na^{+}$  ions. Such an electrode did not show the extended lifetime of one using completely covalently-bound components, but completely covalently-bound membranes lacked selectivity. The reasons for this behaviour may not be entirely straightforward, but the mediator:sensor ratio and mobility of species within the membrane phase are thought to be important contributing factors.

CHAPTER 7.

Mechanistic Aspects of Covalently-Bound

Sensor (CBS) Electrodes.

The theoretical basis of electrode response is now well-established for many types of electrode. The CBS electrodes which have been described so far in this work do not immediately fit into any one of the existing, established categories. In this chapter, results from various studies have been brought together in an attempt to present a picture of the response of the CBS electrode from which some conclusions may be drawn.

#### 7.1 Membrane conditioning.

Results presented in Sections 3.3.1 and 6.3.2 have indicated that conditioning of membranes is important. In particular, the presence of a certain activity and type of ion is important - as discussed for DAPH electrodes. The generation of active ion-exchange sites is necessary for membrane response, and the particular type of site generated may be of some consequence. In addition, a polymeric membrane might be expected to swell slightly when placed in water due to the uptake of solvent. That both PVC and CBS membranes take up water is indicated qualitatively by the development of opacity within the membrane during the conditioning process. The measurement of d.c. resistance of various CBS electrodes (Table 7-1) during the conditioning process indicated a fall of resistance with time. The swelling of the membrane by uptake of water and the subsequent penetration of small cations into the bulk membrane would be expected to produce such a fall in resistance. The polymer itself, when dry, is virtually non-conducting and so there will be no electronic charge -

TABLE 7-1 Effect of conditioning on membrane resistance.

Electrode	Time elapsed, (hrs)				Comments
	0	6	17	29	
73	$6 \times 10^{10}$	$3.7 \times 10^{10}$	$6 \times 10^{10}$	$8.7 \times 10^{10}$	Pure SBS
75c	$5 \times 10^{10}$	$2.8 \times 10^9$	$2.75 \times 10^7$	$6.8 \times 10^6$	
75d	$4.8 \times 10^{10}$	$1.4 \times 10^{10}$	$4.6 \times 10^7$	$8.3 \times 10^6$	
Electrode	Time elapsed, (hrs)				
	0	4	9	23	
74g	$4.8 \times 10^{10}$	$3.4 \times 10^{10}$	$6.2 \times 10^8$	$7.1 \times 10^6$	noisy response
74r	$2.8 \times 10^{10}$	$3.6 \times 10^8$	$1.15 \times 10^8$	$3.1 \times 10^7$	
74s	$2.5 \times 10^{10}$	$1.6 \times 10^9$	$6.5 \times 10^8$	$1.87 \times 10^8$	
74t	$2.85 \times 10^{10}$	$4.3 \times 10^8$	$1.5 \times 10^8$	$3.8 \times 10^7$	
75d <sub>2</sub>	$2.95 \times 10^{10}$	$3.2 \times 10^7$	$6.8 \times 10^6$	$2.5 \times 10^6$	
75e	$5.7 \times 10^{10}$	$1.4 \times 10^7$	$7.2 \times 10^6$	$4 \times 10^6$	
78g	$1.9 \times 10^6$	$5.8 \times 10^5$	$4.5 \times 10^5$	$4.5 \times 10^5$	Anionic

conduction within the membrane. The most functional CBS electrodes had a d.c. resistance in the  $10^6 - 10^7$  ohm range and required up to 48 hours to assume a stable electrode potential and d.c. resistance. That such a long time was required for the conditioning of a CBS electrode when compared to a PVC electrode ( $\sim 4$  hours) may have indicated that the CBS rubber membrane took up water and swelled far less rapidly than PVC-type electrodes. This is likely to have resulted from the 'tighter' nature of the crosslinked polymer in a CBS electrode. The results from this study indicated that a CBS electrode had to be conditioned and that this process probably meant that such an electrode had an ionic charge-conduction mechanism. It must be borne in mind however, that the CBS electrode has a fixed ion-exchange site and so the ion-site complex will be unable to migrate across the membrane as in a liquid membrane or PVC matrix ISE.

## 7.2 Response time behaviour.

The response time of ion selective electrodes depends upon the type of electrode and the conditions of measurement as discussed in Section 3.3.4. Previous studies<sup>162,179,180</sup> have shown that solid state (SS) ISE often show dynamic response times in the millisecond range, liquid ion-exchange membrane electrodes show dynamic response times of the order of 30s or minutes, and that PVC matrix membranes are intermediate.

The dynamic response time of all three types depends upon: <sup>181</sup>

- a) surface ion-exchange;
- b) transport of ions through the diffusion layer to the membrane surface;
- c) bulk transport in or at the membrane surface.

In the case of SS ISE the surface layer is most-important and the ion-exchange sites are fixed, whilst in liquid-membrane or PVC-matrix ISE the bulk membrane must equilibrate and the ion-sites are mobile.

In the comparison of the electrode dynamic response times of an Orion liquid membrane electrode and a CBS electrode at 25°C (Figs. 3-11, 12 and 13, Table 3-8) it was shown that the CBS electrode had a faster dynamic response than the liquid membrane ISE but that it was slower than a solid state ISE. However, the method of measurement would have been unable to detect response times of less than 1 second so it may only be concluded that the response time was significantly less for a CBS electrode than for the Orion 92-20. This may be expected as the CBS electrode has fixed ion-exchange sites and, as such, may be more similar to a solid state ISE than a liquid membrane ISE which has mobile sites.

Previous studies <sup>179,182,182</sup> had indicated that the dynamic response time for glass or liquid membrane ISE increased with decreasing temperature. Thus, the response time behaviour (Sec.3.3.4) of a CBS and Orion 92-20 electrode was

studied at 5, 25 and 50°C. Results indicated that the dynamic response time of both electrodes was significantly slowed at 5°C (Figures 7-1,2 and 3) when compared to their responses at 25°C (see Figs. 3-11,12 and 13). The values for dynamic response times of both electrodes were similar at 5°C showing that the CBS electrode had been comparatively more affected than the Orion. The response times at 50°C (Figures 7-4,5 and 6) were significantly faster for the CBS electrode than for the Orion 92-20 electrode. At this temperature, however, the response of the Orion 92-20 began to deteriorate - presumably due to the increased sensor-leaching experienced at the elevated temperature. The response time of the CBS electrode at 50°C was significantly faster than at 25°C and the response profile showed the presence of maxima on changing sample  $\text{Ca}^{2+}$  activity. The origin of these maxima was unknown, but was also seen with the Orion 92-20 at higher calcium activity. The mean dynamic response time and standard deviation of this figure from six determinations (Table 7-2) indicated that the CBS electrode was generally faster than the Orion electrode and that the CBS electrode results were much more reproducible. Both electrodes showed increases of dynamic response time with decrease of temperature. This variation of response time with temperature indicated that the response time was probably diffusion-controlled<sup>179</sup>. The slowing of response at low temperature suggests that the CBS electrode responds in a

pCo=403

749

$t_{95}$  response time

5°C

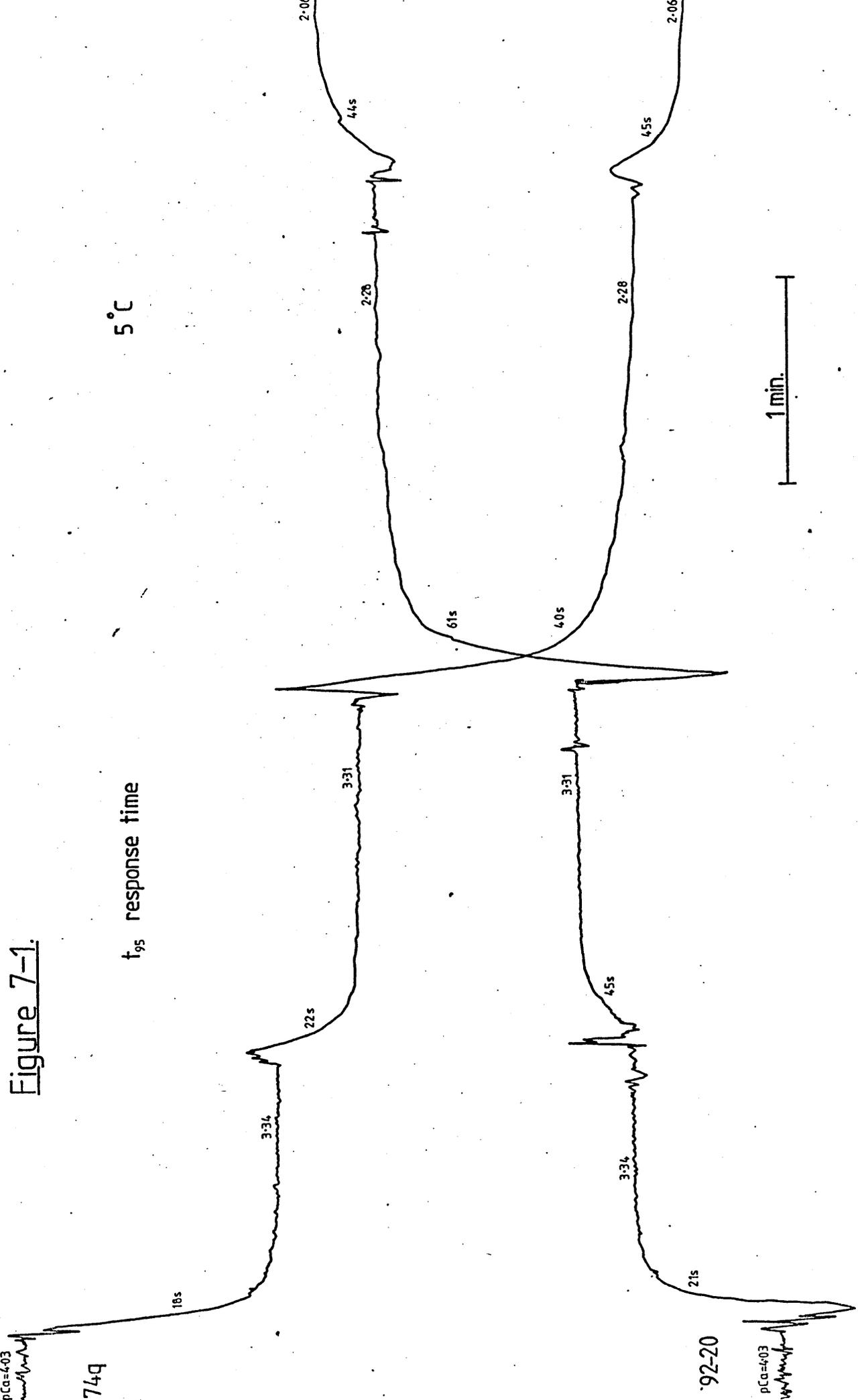


Figure 7-1.

pCo=403

92-20

1 min.

Figure 7-2

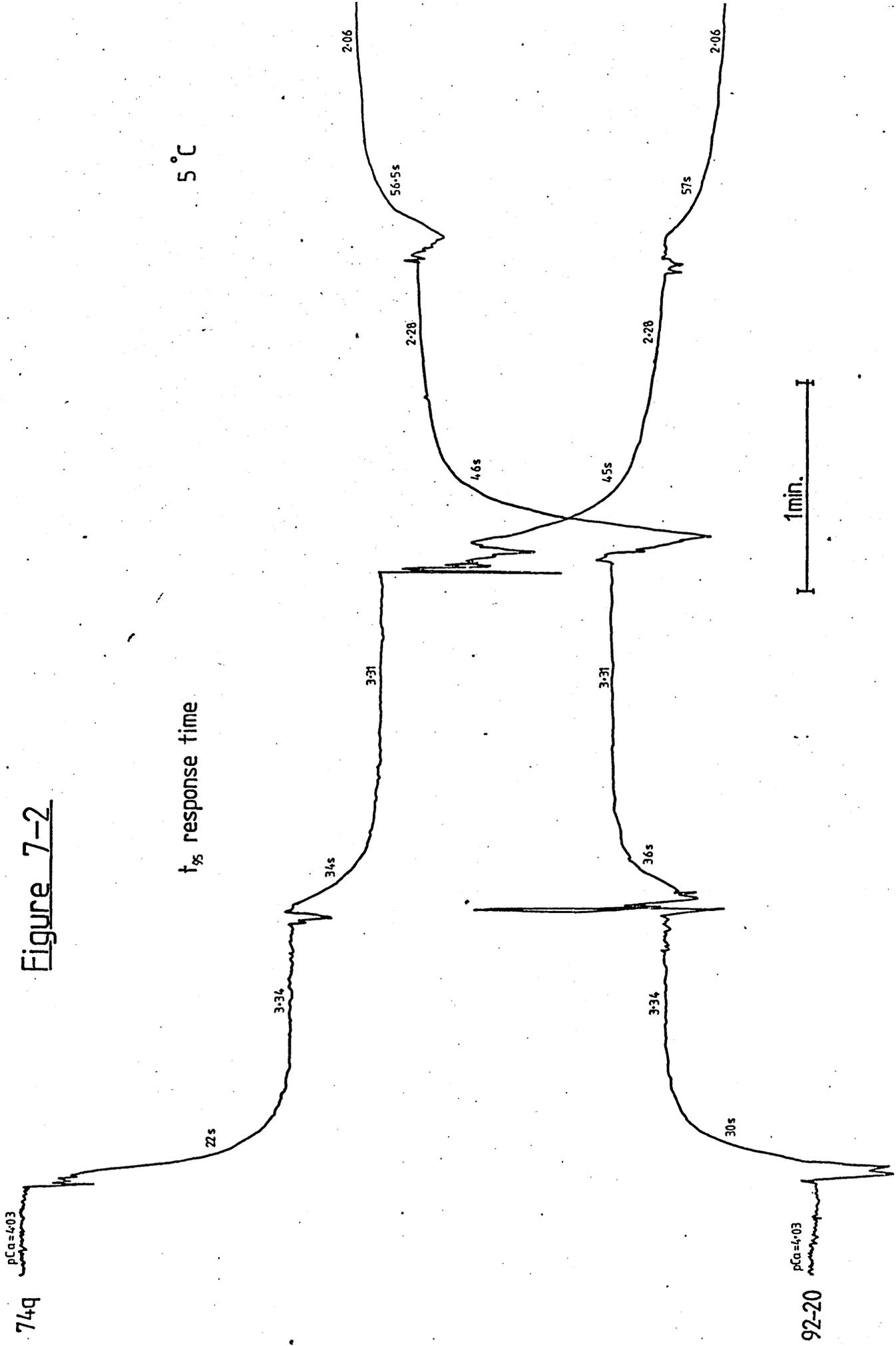


Figure 7-3

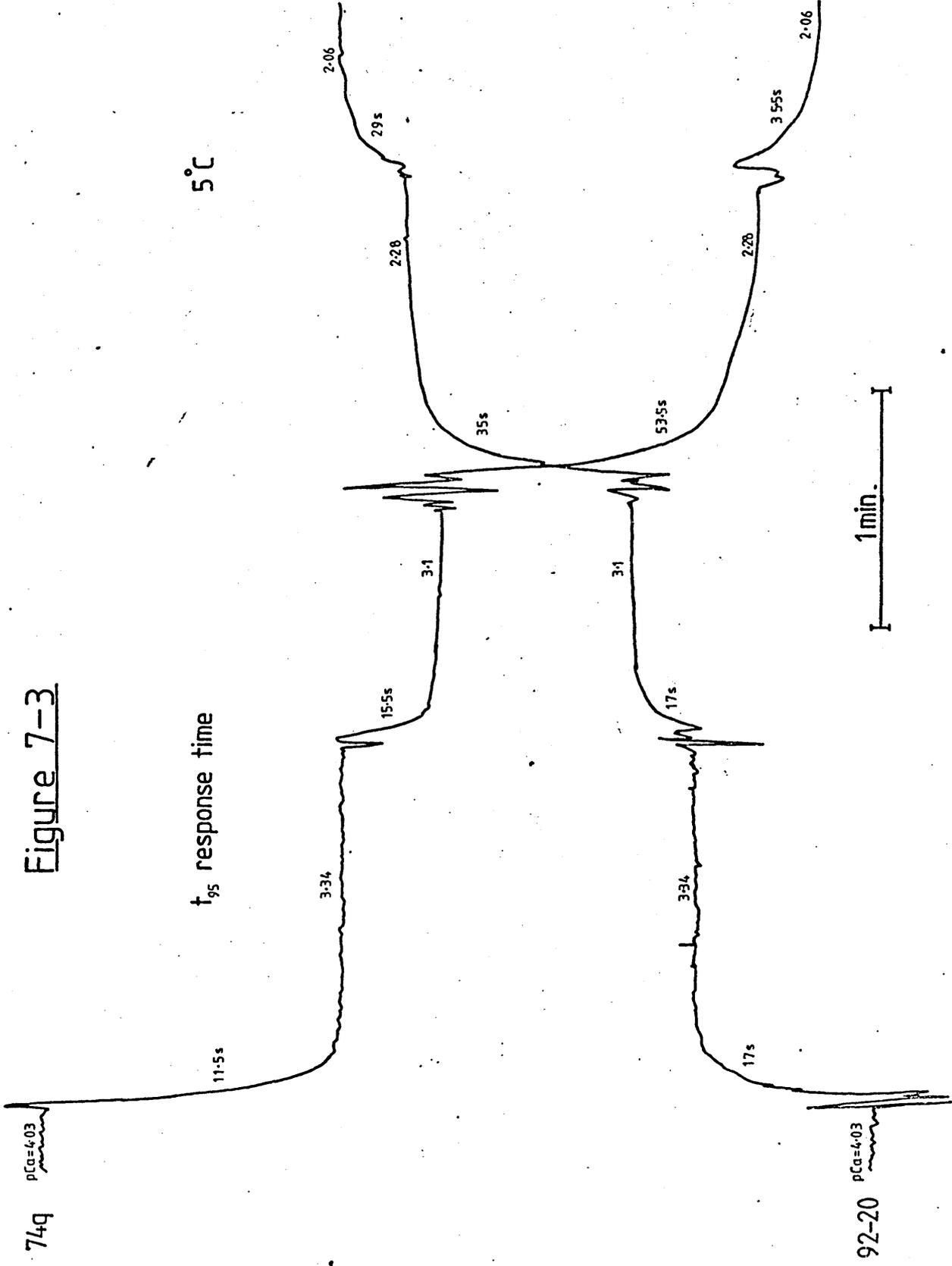


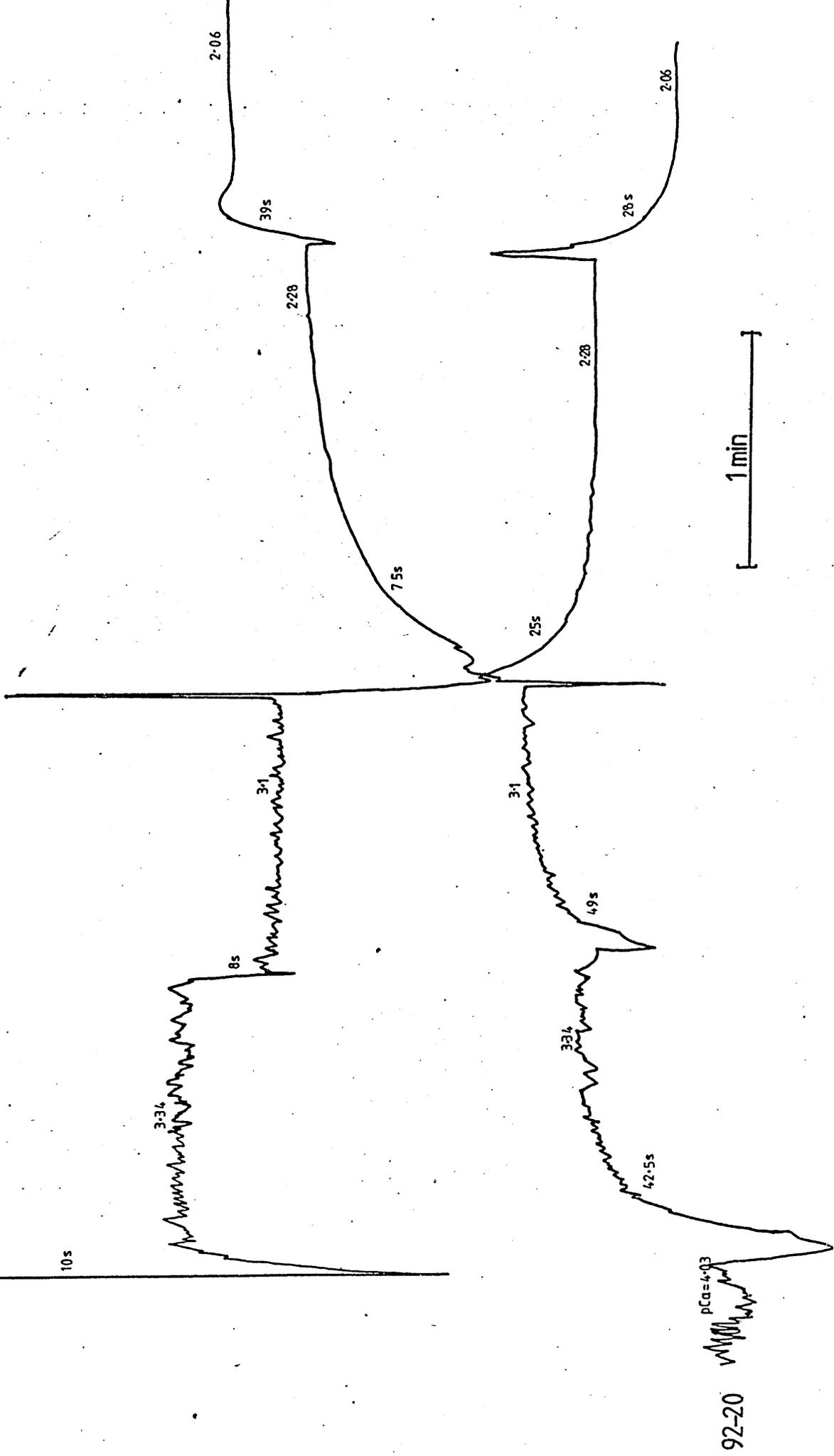
Figure 7-4

PCa=4-03

74g

$t_{95}$  response time

50°C



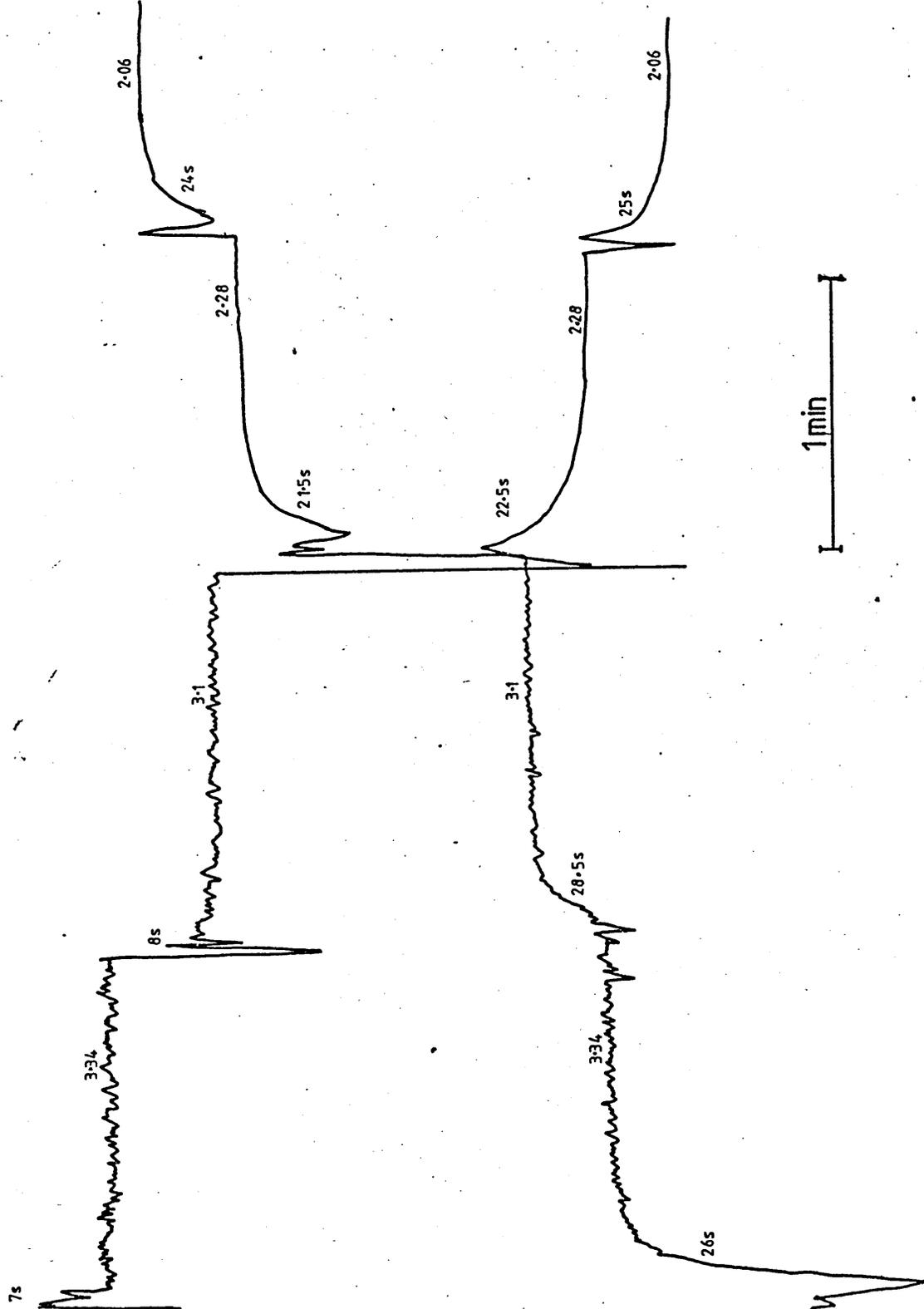
749

PCG=4-03

Figure 7-5

$t_{95}$  response time

50°C



PCG=4-03

92-20

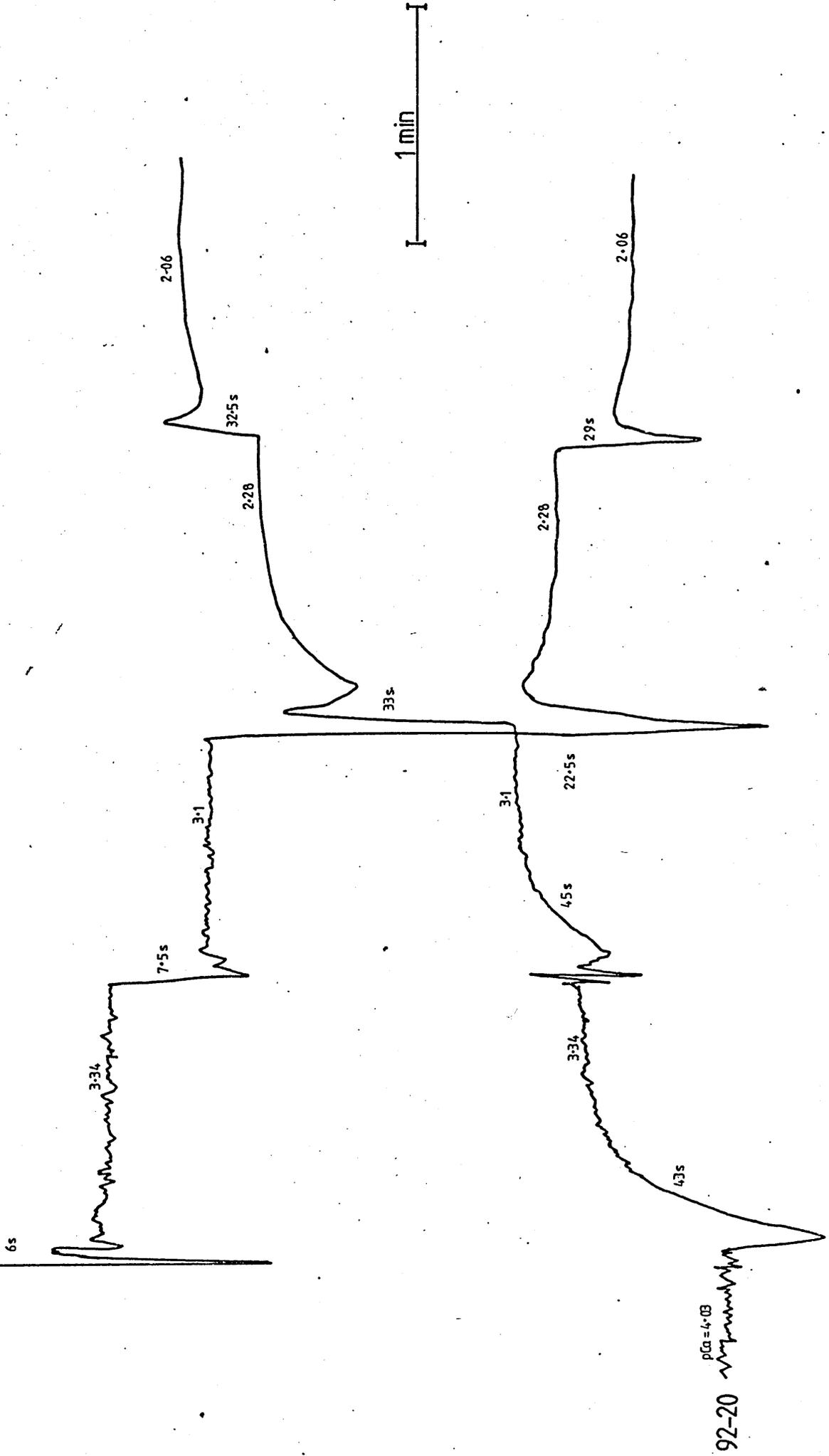
PC# = 4-03

74q

Figure 7-6

$t_{95}$  response time

50°C



PC# = 4-03

92-20

TABLE 7-2. Temperature Dependence of the Electrode Dynamic Response Time.

5 <sup>o</sup> C	Orion	$\bar{x}^*$	19.9	33.9	49.8	46.7
		$\sigma$	10.8	12.5	12.3	11
5 <sup>o</sup> C	CBS	$\bar{x}$	17.8	29.5	48.9	45.6
		$\sigma$	4.8	10.3	9.1	12.5
25 <sup>o</sup> C	Orion	$\bar{x}$	18.7	25.4	28.2	31.6
		$\sigma$	8.3	10.4	10.7	15.5
25 <sup>o</sup> C	CBS	$\bar{x}$	11.5	10.7	12.4	18.4
		$\sigma$	3.6	3.1	4.2	7.8
50 <sup>o</sup> C	Orion	$\bar{x}$	32.4	36.4	40.9	32.9
		$\sigma$	12.4	12.6	23.5	6.4
50 <sup>o</sup> C	CBS	$\bar{x}$	6.75	9.1	24.3	28.6
		$\sigma$	2.5	2.3	2.2	3.1

\* Mean of 6 determinations.

$\sigma$  = standard deviation.

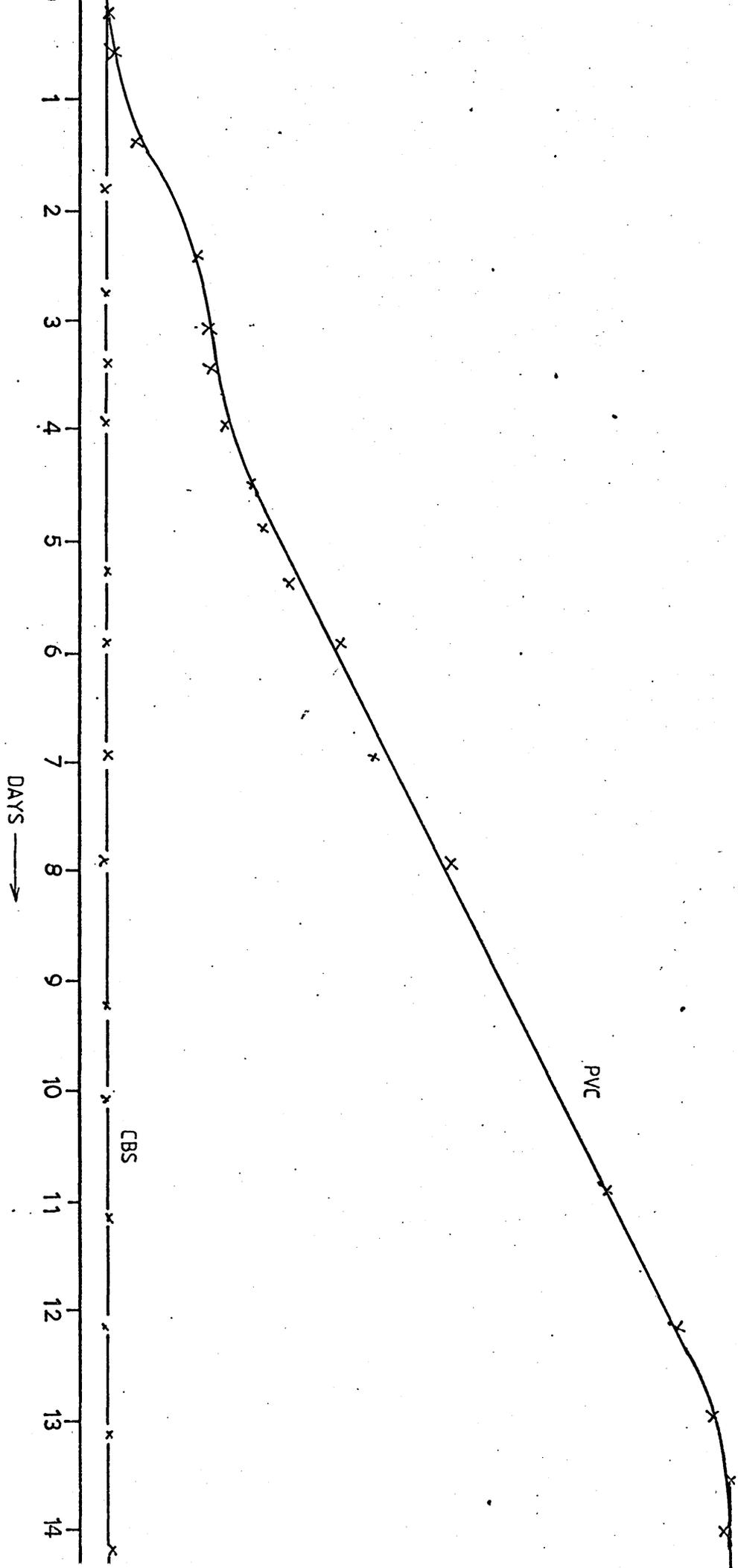
manner similar to glass or liquid membrane ISE rather than solid state ISE.

### 7.3 Radiotracer studies.

The use of radiotracer techniques in the study of ISE response has been limited. In a classical early study<sup>184</sup>, tritium was used to indicate that  $H^+$  ions did not pass through the membrane of a glass electrode. More recently, studies have been carried out using PVC-matrix calcium ISE<sup>140,185,186,187</sup> which have indicated that such electrodes have membranes which are permselective for calcium ions and which are impermeable to chloride ions. An extended study<sup>140</sup> using a  $^{45}Ca$  tracer has shown that the  $Ca^{2+}$  exchange process in a PVC matrix Ca ISE occurs by a one-step process - as opposed to the two or multi-step process occurring in a solid ion-exchanger. Thus, linear Mackay plots<sup>188</sup> were obtained for a PVC matrix Ca ISE indicating a liquid ion-exchanger process was taking place. Curved Mackay plots would have indicated a solid-state ion-exchange reaction at the ISE membrane.

Experiments similar to the above were conducted using CBS sensor membranes and electrodes. Firstly, the permeability of a CBS electrode to  $Ca^{2+}$  ions was investigated. Thus, the internal reference solution of a working CBS electrode was labelled with  $^{45}Ca$  - a weak  $\beta$ -emitter. A Ca sensor unit (PVC tube with the end sealed by a 4.5% TAP membrane), whose response to  $Ca^{2+}$  was Nernstian, was filled with  $1cm^3$  of  $2.5 \times 10^{-4} M CaCl_2$  solution. This solution had an activity of 0.2 mCi and was prepared from a  $^{45}CaCl_2$  solution (2mCi in  $1 cm^3$ , The Radiochemical

Figure 7-7 Membrane permeability comparison



Centre, Amersham, Bucks), by dilution with distilled-deionised water. The sensor unit was then sealed securely with paraffin film and the sensor unit was suspended in  $10\text{cm}^3$  of unlabelled  $10^{-5}\text{M CaCl}_2$ . A similar procedure was carried out for a PVC electrode made using Orion 92-20-02 exchanger and PVC (as previously described). Aliquots ( $25\mu\text{l}$ ) of the outer electrode membrane solution were taken (Oxford Sampler-II Adjustable Micropipette, Oxford Labs. Int. Corp., Athy, Co. Kildare, Ireland), placed on a planchet, dried and counted (G.M. Tube voltage=600V, Scaler 7000, Nuclear Enterprises, Reading, England), using a 40s preset count. Samples were taken at frequent intervals using disposable pipette tips and the results of the permeability study for the two electrode sensors is shown in Figure 7-7. The outer solution showed appearance of  $^{45}\text{Ca}$  after  $1\frac{1}{2}$  - 3 days in the case of the PVC electrode and the attainment of equilibrium after 13 days sampling. These results are in good agreement with those of both Bailey<sup>140</sup> and Craggs<sup>186</sup>. The CBS electrode showed no appearance of  $^{45}\text{Ca}$  in the bathing solution even after 2 months of sampling. This would seem to indicate a difference in the mode of operation of the two types of electrode. The observation that 2 months passed with no passage of  $^{45}\text{Ca}$  through the CBS membrane, even in the presence of a favourable concentration gradient, may suggest that it was not merely a 'slowing down' of the trans-membrane  $\text{Ca}^{2+}$  passage occurring, apparently there was no  $\text{Ca}^{2+}$  passage occurring. This result,

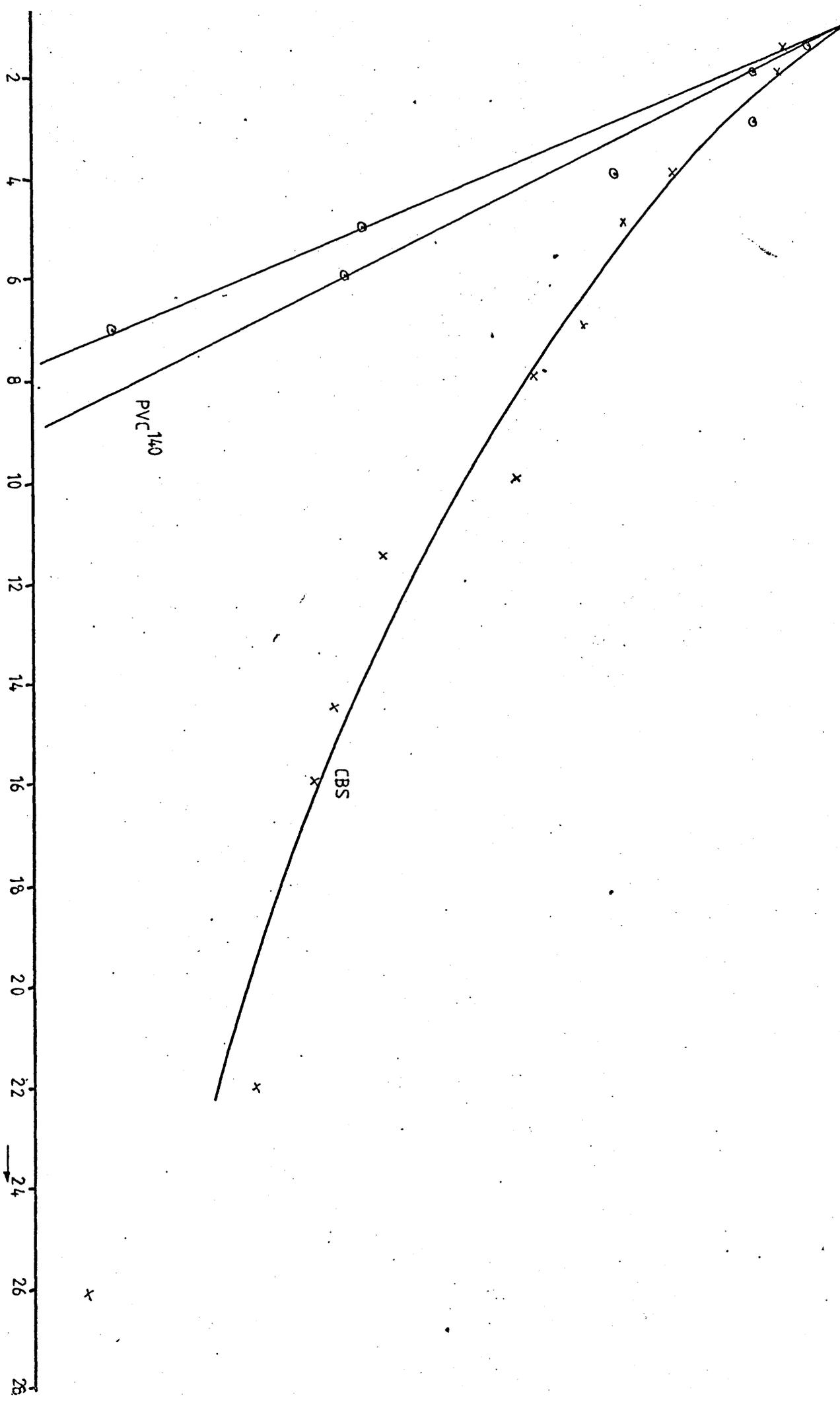
TABLE 7-3. Mackay Plot data.

1	2	3	4	5	6	7	8
Time (hours)	Volume (25 $\mu$ l.)	Counts.sec. <sup>-1</sup> 25 $\mu$ l. <sup>-1</sup>	Solution activity, t (3 <sub>t</sub> x 2 <sub>t</sub> )	Total Activity, t (4 <sub>t=0</sub> - $\sum_{i=0}^{t-1}$ 3 <sub>i</sub> )	Membrane activity, t (5 <sub>t</sub> - 4 <sub>t</sub> )	A <sub>mem</sub> /A <sub>TOT</sub> (6/5)	F (7/7equil.)
0	400	132.9	53160	53160	0	0	0
.083	399	129.2	51551	53027	1476	.03	.064
.25	398	127.1	50586	52898	2312	.04	.085
.5	397	126.2	50101	52771	2670	.05	.106
1	396	121.8	48233	52645	4412	.084	.179
1.5	395	115	45425	52523	7098	.135	.287
2	394	114.2	44995	52408	7413	.14	.298
4	390	105.5	41145	51969	10824	.21	.447
5	388	102.1	39615	51752	12137	.24	.51
7	386	99.2	38291	51549	13258	.26	.55
8	385	96.7	37230	51450	14220	.28	.60
10	383	95.4	36538	51252	14714	.29	.62
11 $\frac{1}{2}$	383	87.8	33540	51164	17624	.34	.72
14 $\frac{1}{2}$	380	87.1	33098	50997	17899	.35	.75
16	379	86.7	32860	50910	18050	.355	.76
22	377	84.9	32007	50734	18727	.369	.79
26	375	80.2	30075	50569	20494	.405	.86
32	373	80.8	30138	50408	20270	.40	.85
106	372	74.7	27788	50327	22539	.45	.96
143	370	72.3	26751	50182	23431	.47	1
263	368	71.6	26349	50041	23692	.47	1

and the observation that d.c. resistance decreases on conditioning of a CBS electrode in  $\text{Ca}^{2+}$  media may seem contradictory. It may be possible that ion-exchange is occurring in the membrane surface layer with ionic charge-conduction through the membrane much in the same way as seen with glass electrodes. The immobility of both the glass electrode exchange sites and the covalently-bound sensor sites would preclude ion transport across the membrane as an ion-site moiety.

Bailey<sup>140</sup> has not only shown that the PVC matrix Ca ISE was permeable to  $\text{Ca}^{2+}$  ions, but has also shown that such a membrane acted as a liquid rather than as a solid ion-exchanger. This was inferred from the linear Mackay plots obtained with such membranes. Thus, in this study, CBS membranes were subjected to a similar series of experiments to determine whether such membranes acted as liquids or solids i.e., showed linear or curved Mackay plots, respectively. Discs of CBS membranes (9mm dia.) were soaked in distilled-deionised water for 3 days and then placed in a calcium tracer solution ( $10\text{cm}^3$ ,  $2.5 \times 10^{-6}\text{M}$ ,  $2\mu\text{Ci } ^{45}\text{CaCl}_2$ ). The uptake of  $^{45}\text{Ca}$  into the membrane from the solution was monitored by taking  $25\mu\text{l}$  samples, drying them and counting under the same conditions as used for the  $^{45}\text{Ca}$  permeability study. The corrected results were then converted to results which could be used for production of a Mackay plot (Table 7-3) of  $\log(1-F)$  vs. time. The results for a pure SBS membrane indicated no tendency to exchange  $\text{Ca}^{2+}$  ions. The

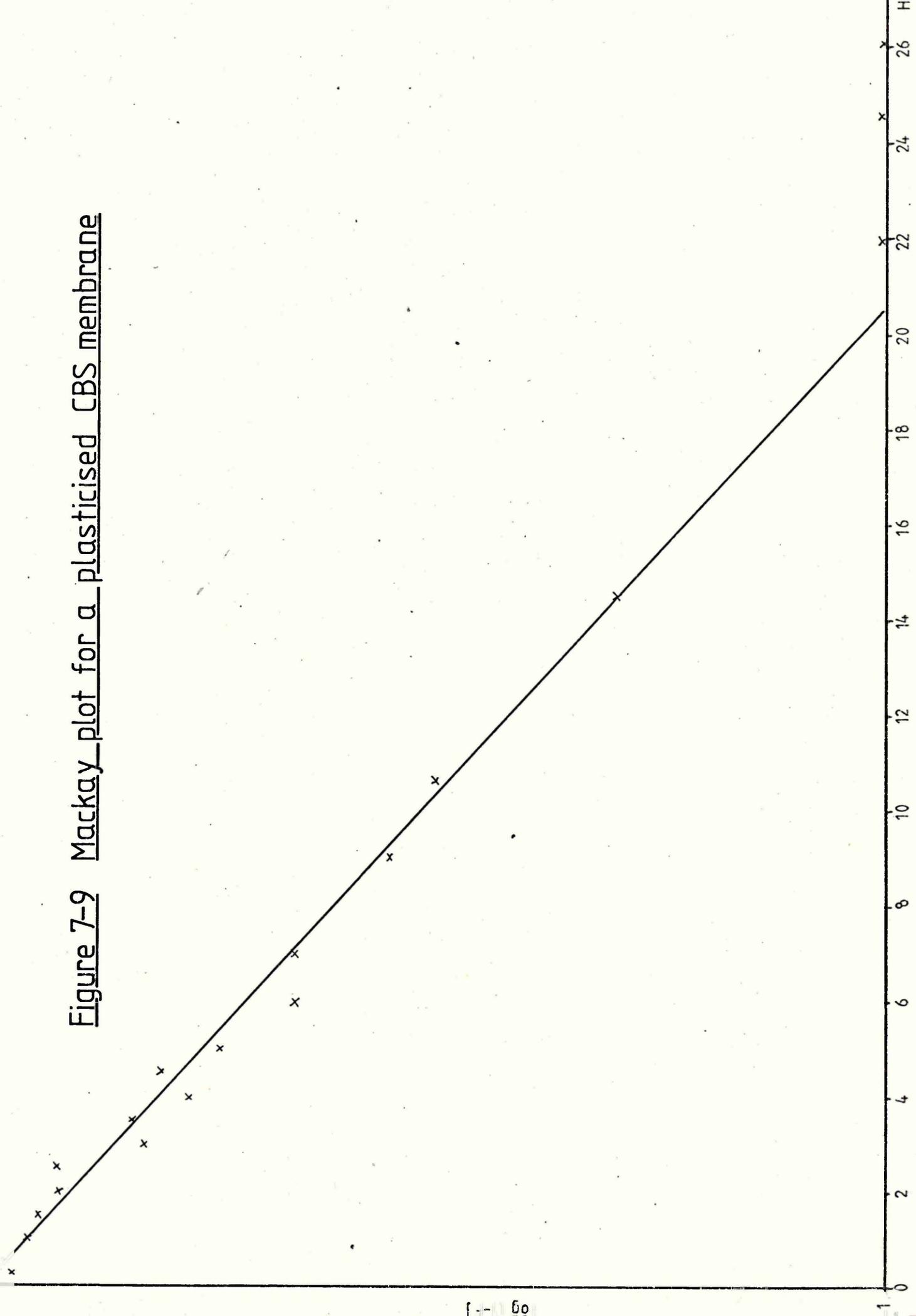
Figure 7-8 Mackay\_plots for PVC and CBS membranes



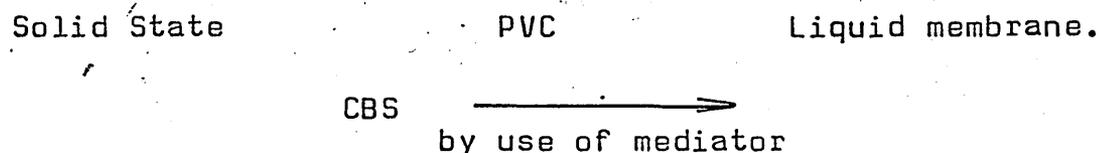
Mackay plot produced for a 5% DAPH membrane (Figure 7-8) showed an initially-rapid uptake of  $\text{Ca}^{2+}$  followed by a much slower exchange process yielding a curved plot. Comparison of this plot with one from a PVC electrode<sup>140</sup> shows the distinctly-different profiles. In the case of the CBS membrane, the final  $\text{Ca}^{2+}$  uptake level was not reached for more than 36 hours compared with the 8 to 10 hours seen with a PVC electrode. The curved plot obtained for the CBS membrane would seem to support earlier suggestions that the electrode response was principally affected by the membrane surface properties. Thus, the membrane was not acting as a liquid ion exchanger - more as a solid ion-exchange disc. The rapid initial uptake of  $\text{Ca}^{2+}$  may reiterate the importance of the surface and concur with the observation of a rapid electrode dynamic response time.

A similar experiment was performed using a CBS membrane containing 5% DAPH and 25% DOPP. This membrane had yielded the least mechanically-strong CBS membrane, but had resulted in the most-selective Ca ISE. Use of the  $\text{Ca}^{2+}$  ion uptake results, in a Mackay plot, yielded a straight line (Figure 7-9) whose intercept was at 12 to 14 hours. This indicated a behaviour somewhat similar to a PVC matrix membrane (straight line plot, intercept 8-10 hours) but markedly different from that of a CBS electrode containing 5% sensor with no mediator. This suggested that a CBS and a CBS membrane with mediator operated by a different response mechanism. When compared to

Figure 7-9 Mackay plot for a plasticised CBS membrane



a CBS electrode with sensor only (which behaved as a solid ion-exchange disc), the plasticised CBS membrane behaved more like a 'liquid' ion-exchange membrane electrode. This more 'liquid' structure was able to exploit not only the advantages of a covalently-bound ion selective sensor group, but also the benefit of the presence of a mediator in sufficient quantity to influence ion-exchange selectivity. The presence of entangled liquid mediator and the subsequent plasticisation may have provided an additional transport mechanism via the solvation of ions in the mediator. Thus, we may envisage a spectrum of electrode physical and exchange properties such as:



The use of a CBS electrode with and without a mediator may enable benefits from other systems to be brought together.

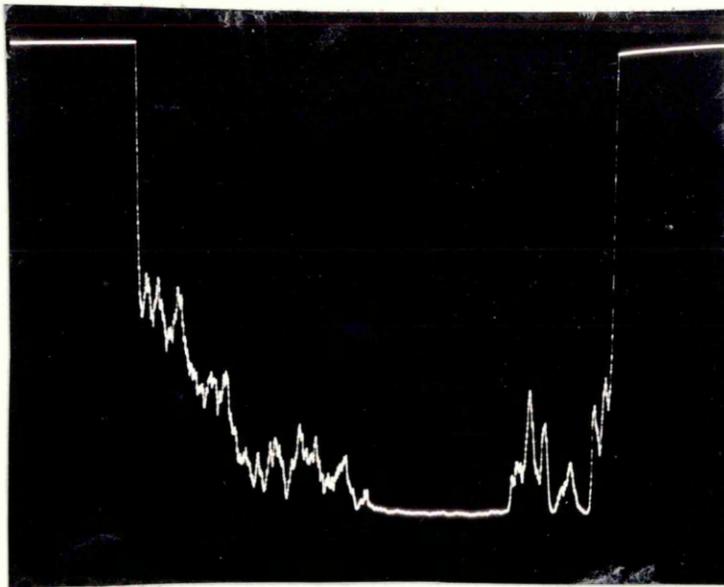
#### 7.4 Surface Analysis.

It seems rather surprising that the surfaces of ISE have received little study, particularly as it is the surfaces which largely determine the overall membrane response. Griffiths<sup>99</sup> investigated the pores in the surface of PVC matrix Ca ISE using optical microscopy but concluded little from the results. Pungor's group<sup>189,190</sup> have made use of electron microscopy, electron microprobe analysis and photoelectron spectroscopy in the investigation of the surface morphology of some silicone-rubber matrix ISE. In the work described here, scanning electron

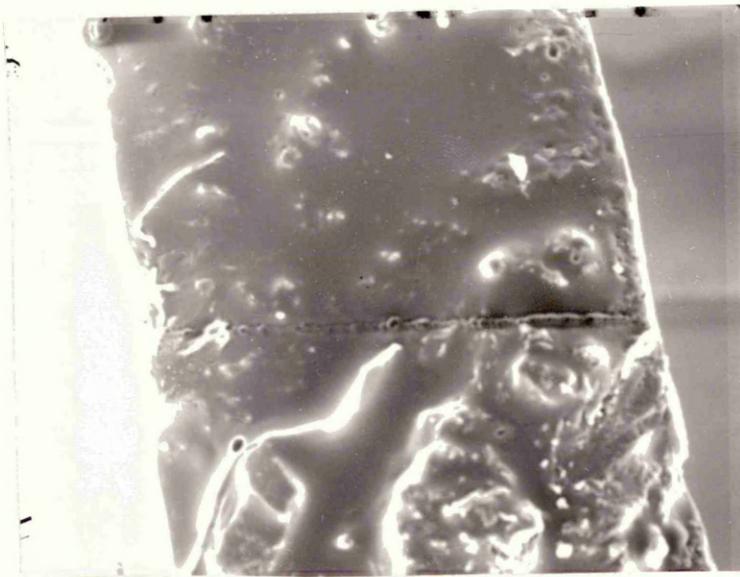
microscopy and energy dispersive X-ray analysis have been used to analyse the surfaces of a CBS membrane.

Thus, a disc of CBS membrane was soaked for 10 days in  $10^{-1}$  M  $\text{CaCl}_2$  solution at  $25^\circ\text{C}$ . This disc was then thoroughly washed with distilled-deionised water and dried. After immersion in liquid nitrogen for about two minutes the membrane was broken along a diameter. The sections of this membrane were then mounted and sputtered with gold such that the 'interior' of the CBS membrane could be examined and analysed. The use of a scanning electron microscope (SEM) (Philips P SEM500, Cambridge, U.K.) fitted with an energy-dispersive X-ray analyser (EDAX) (EDAX Model 711) enabled the morphology and the chemical microstructure of the membrane to be investigated. Thus, areas of interest in the polymer were both photographed using the SEM and elemental line scans for both Ca and Cl were made across the same area of the sample using the EDAX microprobe. The use of magnifications greater than 1500 x was avoided as it was not necessary and led to excessive 'burning' of the membrane.

An electron micrograph of the membrane followed by an elemental line scan for Cl from top to bottom through the centre of the membrane yielded the picture and traces shown in Plate 7-10 (a and b). The two photographs are superimposable - the line across the membrane in 7-10b indicates the position of the EDAX scan (7-10a). The EDAX Cl elemental line scan (7-10a)



a.



b.

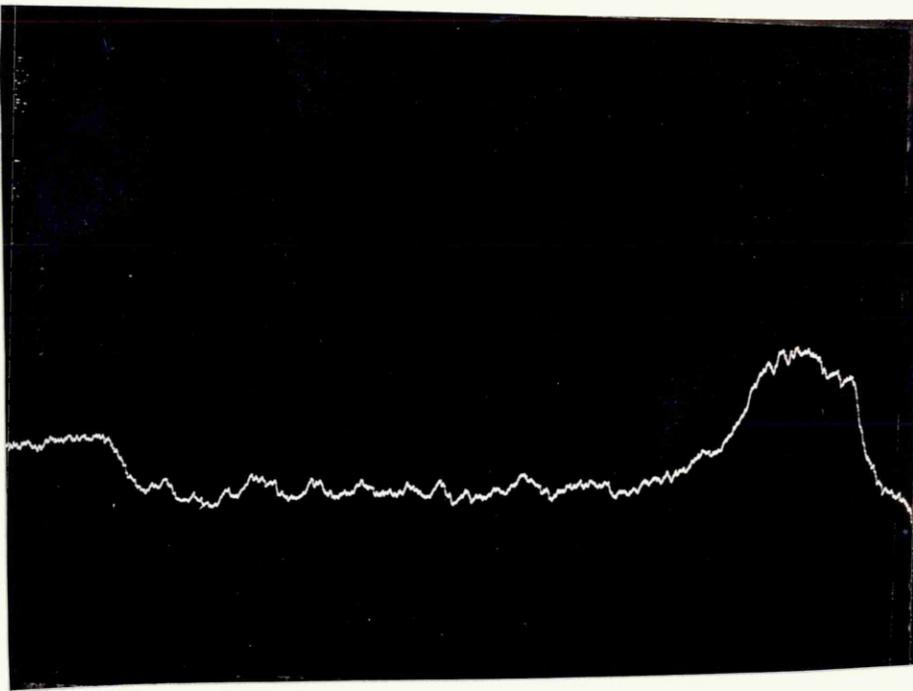
Plate 7-10 Cross-section through a CBS membrane

a. EDAX Cl line scan

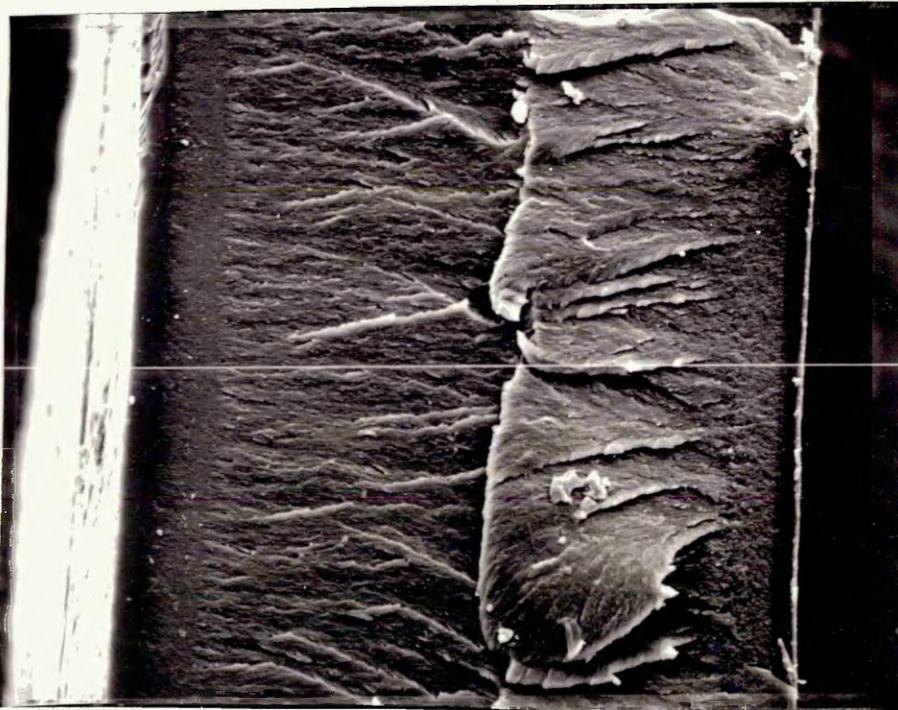
b. electron micrograph,  $\times 120$

shows the high concentration of Cl at and near the surface of the membrane with a fall to zero Cl at the centre of the membrane. Thus, Cl<sup>-</sup> ions are concentrated at the membrane surface and do not exist at a detectable concentration in the membrane centre. (The reason for the high Cl count off the edge of this particular membrane was that the sample was mounted in PVC).

The use of the Cl line scan/SEM method indicated the feasibility of using this technique for the study of CBS membrane morphology/composition relationships. Samples (0.5mm thickness) were mounted using a cyanoacrylate adhesive and sputtered with gold. Plate 7-11a shows a Ca line scan across the membrane thickness (Plate 7-11b) at a magnification of 130 x. The Ca line scan shows a much higher Ca concentration at the sample edges than at the sample centre. Despite the very low count-rate through the membrane centre, the EDAX technique has insufficient sensitivity to confirm absence of calcium from the centre. That there is a comparatively much lower concentration away from the edge of the membrane is further demonstrated in Plate 7-12. In this, the magnification has been increased to 1120 x and the micrograph (b) clearly shows a morphological difference in the surface layer which was not so obvious at a lower magnification. This surface layer is about 50  $\mu$ m thick and corresponds exactly with the maximum seen in the Ca line scan (Plate 7-12a) over the same area and at the same magnification. The membrane away from the edge shows a baseline Ca line scan suggesting that Ca is concentrated



a.

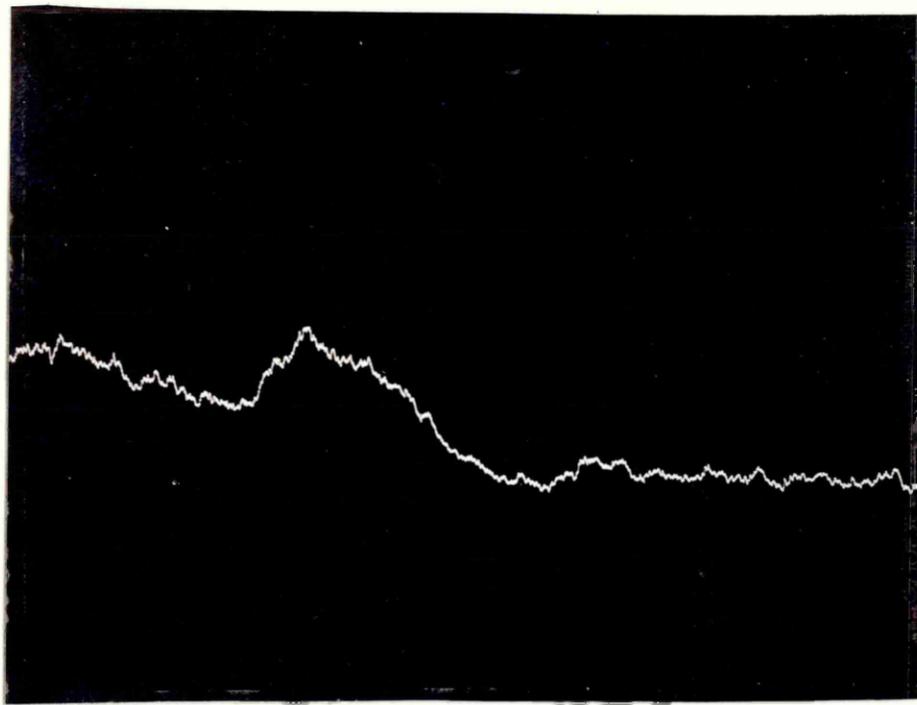


b.

Plate 7-11 Cross-section through a CBS membrane

a. EDAX Ca line scan

b electron micrograph,  $\times 130$



a.



b.

Plate 7-12 Cross-section through a CBS membrane

a. EDAX Ca line scan

b. electron micrograph,  $\times 1120$

in the 50  $\mu\text{m}$  surface layer. The reason for this different surface layer morphology and its Ca content may lie in the uptake of water into the membrane. This 'hydrated layer' is then capable of taking up  $\text{Ca}^{2+}$  ion onto the active ion-exchange sites. The baseline level of Ca away from the membrane edge results from the low hydration /swelling of the bulk membrane. This 'picture' of the membrane of the CBS electrode is, in many ways, similar to that of the hydrated glass pH electrode membrane.

#### 7.5 Conclusions.

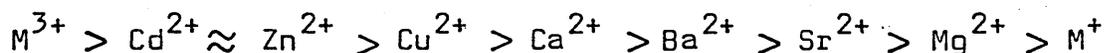
From the various studies, it is possible to draw several tentative conclusions with regard to the response mechanism operating in the CBS electrode. In the absence of a plasticiser, the membrane acts as a solid ion-exchange disc which has a surface layer rich in  $\text{Ca}^{2+}$  ions compared to the membrane bulk. Passage of  $\text{Ca}^{2+}$  ions from one side of the membrane to the other may occur at a very low level, but more likely, there is no passage of  $\text{Ca}^{2+}$ . This results in a mechanism similar to that of a glass electrode. Thus,  $\text{Ca}^{2+}$  ion exchange occurs in the hydrated surface layer and bulk membrane conduction is by smaller more mobile ions. The exclusion of  $\text{Ca}^{2+}$  ions from the bulk of the membrane by virtue of the poor bulk-membrane mobility for such a large cation may be responsible for the low selectivity of such electrodes for  $\text{Ca}^{2+}$  in the presence of other cations.

That is to say, in an ion-exchange electrode of the glass electrode type the higher mobility of monovalent ions over

divalent ions will to a large extent offset the preference of the ion-exchange site for calcium ion, resulting in less than optimal  $\text{Ca}^{2+}/\text{M}^+$  selectivity. In the presence of a plasticising (or solvent) mediator the above mechanism was apparently modified. Thus, the mediator plasticised the membrane causing it to become more 'liquid'-like. This more 'liquid' structure would allow greater mobility of divalent cations (e.g.  $\text{Ca}^{2+}$ ) in the bulk membrane providing possibly an additional transport mechanism i.e. solvation. This enhanced mobility of divalent cations may enable more-effective competition with monovalent cations allowing fuller advantage to be taken of the inherent selectivity of the ion-exchange site. Further studies into the mechanism of CBS electrode response and the effect of mediator inclusion may yield electrodes whose physical and electrochemical performance can be tailored to a particular requirement.

## General conclusions.

From the researches undertaken for this thesis it has become apparent that calcium ion selective electrodes (ISE) may be fabricated from a polymer membrane in which the sensor groups are covalently-bound. Such an electrode, by virtue of its covalently-bound sensor, has been found to show advantageous properties in terms of operational lifetime, response time and ability to withstand hostile environments encountered with 'real life' samples. Optimal performance was obtained from electrode membranes made from styrene-b-butadiene-b-styrene (SBS) triblock elastomer crosslinked with 4.5% m/m triallylphosphate (TAP) and then hydrolysed in 5% m/m methanolic KOH. The mechanism of response of this new type of electrode is, apparently, in many ways analogous to that of a glass electrode. That is to say,  $\text{Ca}^{2+}$  ions have been found not to pass through the membrane, but to be exchanged in a swollen, hydrated surface layer of the membrane. The selectivity of electrodes produced using TAP as crosslinking agent was poorer than for 'state of the art' Ca ISE. They showed the following order of selectivity:



which is in agreement with the absorption sequence for an ion-exchange resin made from hydrolysed poly(triallyl phosphate). Improvements in selectivity were not effected by the incorporation of either trioctyl phosphate, tri (10-undecenyl) phosphate or diallyl phenylphosphonate (DAPP) as crosslinking

monomers. The reasons for this are thought to lie in the small overall change in sensor group chemistry introduced by the above changes of monomer. The general lack of bulk membrane mobility of  $\text{Ca}^{2+}$  ions in the above systems using polymers which are extensively crosslinked is thought to contribute to the disappointing selectivity especially with respect to the more mobile monovalent cations. In addition, the absence of a solvent mediator is unlikely to result in exceptional calcium selectivity.

The incorporation of a mediating function into the membrane would appear mandatory for an improved selectivity. The use of a covalently-bound mediator was shown to be possible but without extensive optimisation no firm conclusion as to the viability of this approach can be made. The effect of crosslinking with both sensor and mediator was to 'tighten' the polymer network which resulted in a decrease of ionic mobility within the membrane phase and apparently hindered selectivity. The low mediator:sensor ratio achieved meant that little effect was expected and the low level of sensor used was not conducive to good electrode response. Thus, the role of a covalently-bound mediator must be carefully controlled. Primarily it should not crosslink the polymer matrix but should be capable of creating pendant, mediating functional groups, e.g. phosphonates, able to influence electrode selectivity. Analogues of dioctylphenylphosphonate may be attached by the use of a monofunctional monomer which would not result in crosslinking.

Synthesis of such phenylphosphonic acid esters would not be difficult. Secondly, an increase in divalent ion mobility within the membrane phase would seem necessary to enable full use of the sensor-mediator selectivity enhancement. The use of a 10: 1 mediator:sensor ratio is often recommended and the control of crosslinking would be necessary to enable incorporation of those high levels of co-monomer. Further investigation into the possibility of covalently binding both sensor and mediator groups into a polymer matrix should prove profitable - not merely in the development of ISE. For ISE, the use of alternative polymer matrices enabling the alteration of such variables as sensor concentration, divalent ion mobility and mediator group interaction should be investigated. The use of silicone elastomers with a known, low level of pendant unsaturation (e.g. 5-10% pendant vinyl) might be expected to give more control over membrane properties. The reaction of all these pendant reactive centres during membrane production would yield more-stable membranes which would, in turn, result in electrodes with longer lifetimes. The use of materials designed specifically for the purpose of acting as ISE membranes can only be of advantage.

The use of a covalently-bound sensor in conjunction with an entangled solvent-mediator has proved useful. The incorporation of 5% m/m diallylphosphoric acid (DAPH) sensor has enabled the hydrolysis step in membrane production to be

eliminated. The incorporation of 25% m/m dioctyl phenylphosphonate solvent-mediator into a membrane containing 5% DAPH sensor has yielded a calcium ISE showing favourable selectivity. In such an electrode the glass electrode-type mechanism is thought not to have been operating and the membrane acted more like a liquid membrane. This 'liquid' membrane appeared to facilitate mobility of calcium ions within the membrane and the 5: 1 mediator:sensor ratio ensured a favourable interaction between the ion-site and the mediator. In addition, the solvent may have provided a mechanism for solvation and transport of  $\text{Ca}^{2+}$  ions within the membrane. The use of a covalently-bound sensor and an entangled mediator is worthy of further study as this approach would enable the production of selective ISE. However, it is felt unlikely that electrode lifetime would be markedly enhanced by the use of a covalently-bound sensor in such a system as the loss of mediator by leaching would then become the limiting factor in electrode lifetime. The use of covalently-bound analogues of the optimal entangled mediators may yield further valuable information and, ultimately, better electrodes. The use of a mixed system in which one mediator is covalently-bound and another entangled should not be overlooked. The future use of functionalised polymers will doubtless increase with use in such diverse applications as catalyst and enzyme supports and in industrial extractions and separations. Development of such materials for their use

in ion selective electrodes generally, and not just for calcium ISE, should be investigated as a matter of course.

Electrodes such as that for nitrate which, with an increased lifetime would find greater use in continuous monitoring applications, would be particularly favoured for study. Not only might such an approach yield long-life ISE with good selectivity, but it would furnish greater understanding of electrode response mechanisms and the role of the solvent mediator in polymer matrix ISE.

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*A. T. Ellis*

APPENDIX 1

BASIC Program for the calculation of activity coefficients.

```
/LOAD USEBASIC
010DIMZ(100),I(100),H(100)
020PRINT'THIS PROGRAM CALCULATES THE'
030DIMG(100)
040PRINT'ACTIVITY COEF'
050PRINT''
060PRINT'TO EXIT FROM PROGRAM ENTER ZERO'
070PRINT'LINES OF DATA'
080PRINT''
090PRINT'HOW MANY LINES OF DATA,MAXIMUM OF 100/'
100INPUTN
110IFN=0THEN560
120MATZ(N)=(0)
130MATI(N)=(0)
140MATH(N)=(0)
150MATG(N)=(0)
160F=2
170S=1
180PRINT 'INPUT Z OF EXCESS ION'
190INPUTT
200PRINT'INPUT CONC OF EXCESS ION'
210INPUTV
220PRINT'INPUT THE CONCS OF THE CA IONS'
230MATINPUTZ(N)
240FOFX=1TON
250U=Z(X)
260V1=U*2
270V2=T*U
280V=V1+V2
290D1=F**2
300D2=S**2
310D3=T**2
320E1=D1*U
330E2=D2*V
340E3=D3*W
350H1=E1+E2+E3
360H=H1/2
370I(X)=H
380NEXTX
390PRINT'CONC', 'I', 'GAMMA', 'J'
400FOFM=1TON
410A=0.2*I(M)
420E=SGF(I(M))
430E1=1+E
440C1=.511*E
450C=C1/E1
460D=C-A
470Z=2
480E=Z**2
490F=D*E
500G1=-F
510G=10**G1
520J=G*Z(N)
530PRINTZ(N),I(M),G,J
540NEXTM
550GOTO60
560END
```

Appendix 2.

Course of Study

- Electroanalytical Chemistry - Part-time M.Sc. in Instrumental Analysis.
- Dr. L. Ebdon, Sheffield City Polytechnic
  - 8 hours

Papers published and presented

a. Published.

Ebdon, L., Ellis, A.T. and Corfield, G.C., Analyst, 1979, 104, 730.

Ellis, A.T., Corfield, G.C. and Ebdon, L., Analyt.Proc., 1980, 17, 48.

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b. Presented.

Research Colloquium, Sheffield City Polytechnic, 28th March, 1978. A.T. Ellis.

Research and Development Topics Meeting of the Analytical Division, RSC. Heriot-Watt University, 5th July, 1979. A.T.Ellis.

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