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Nitrate Selective Electrodes Containing Immobilised Ion Exchangers

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Nitrate Selective Electrodes
Containing Immobilised Ion Exchangers

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Abstract

Nitrate Selective Electrodes Containing Immobilised Ion Exchangers

Nicholas Charles Frampton

A range of ion selective electrodes (ISEs) for the determination of nitrate has been produced using polymeric membranes containing immobilised quaternary ammonium salts as the ion exchanger. The use of the conventional solvent casting technique gave rise to a relatively low cross-link density, two sided response and poor thickness control. The development of a hot pressing technique resolved all these problems and would readily suit large scale manufacturing. In this work poly (acrylonitrile-butadiene) (NBr) was selected as the membrane matrix and was robust, gave enhanced selectivity coefficients and extended membrane lifetime. The best electrode fabricated contained 6.5% m/m triallyloctylammonium bromide, 7.2% m/m dicumyl peroxide and 39.7% m/m 2-nitrophenyloctyl ether in a 50% ACN content NBr polymer matrix. The electrode had a lifetime in excess of 665 days and the response to nitrate was Nernstian in the range 1×10^{-1} to 1×10^{-4} mol dm⁻³ of nitrate. The limit of detection was 4.5×10^{-5} mol dm⁻³ and the selectivity coefficient $k_{NO_3^-, Cl^-}^{pot}$ was 5.3×10^{-3} . The immobilised ion exchanger membrane electrode³ offered superior lifetime and mechanical strength.

The cross-link density of the membranes was determined by solvent swelling and the use of the Flory-Rehner equation. The role of cross-link density upon the electroanalytical properties of membranes was investigated in the range 0.6×10^{-5} to 11.0×10^{-5} mol cross-link cm⁻³. The membranes were studied using electron microscopy and the conditioning process monitored using ion exchange chromatography. Two different response mechanisms were proposed dependent on the membrane composition and the inclusion of solvent mediator.

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CHAPTER 1

Introduction

1.1. Nitrate in the Environment

1.1.1 Eutrophication of Lakes and Rivers

The eutrophication of lakes and rivers is of great concern to environmentalists and the public at large. It is predicted that as we move into the "green" decade greater efforts to reverse such effects will be demanded. Eutrophication occurs as a result of the introduction of nutrients such as nitrogen and phosphorous into the river system. The nutrients cause rapid growth of both algae and other aquatic plants which, when they die and decompose, create a significant reduction in dissolved oxygen. There is a marked difference between the behaviour of lakes and that of rivers in this respect, the latter being far more tolerant to the introduction of nutrients [1]. This is due to the more turbulent nature of rivers causing reoxygenation. Accordingly, rivers have demonstrated the ability to recover quickly from the effects of eutrophication.

Although the issue of eutrophication of lakes and rivers is very topical, concern has existed for a considerable period of time. In 1947 [2], interest was focused on the subject of the intentional fertilisation of waters using nutritive substances especially phosphorous and nitrogen. A list of some 20 or so lakes from eight different countries were referenced with varying degrees of pollution and eutrophication recorded. Fish, such as trout, (*salmo salvelinus*) are good indicators of water quality and in poor quality water can not survive. Coarse fish have been shown to be much hardier and in many areas have replaced the perhaps more desirable *salmo salvelinus* species. Perhaps the

most widely publicised case of eutrophication occurred in the Great Lakes with the phrase 'Lake Erie is dead' being coined by protesters [3]. The "death" of the lake occurred as a result of eutrophication caused by the flow of nutrients via a combination of domestic, industrial and agricultural drainage. In 1918 [3] it was recorded that the flow of industrial waste was insufficient significantly to affect water quality. By the 1950's a pollution problem had been recognised which ultimately gave birth to the historic Great Lakes Water Quality Agreement of 1978. The agreement between Canada and the United States of America was signed at Ottawa on 22 November 1978 and was one of the earliest dealing with cross boundary eco-systems. The control of nutrients was covered by Clause E in Article III - "These waters should be free from nutrients directly or indirectly entering the waters as a result of human activity in amounts that create growths that interfere with beneficial uses." This was further defined in Annex EB 1-B-Z where the maximum concentration of un-ionized ammonia was stated as 20mg litre^{-1} for the purpose of protection of aquatic life. The maximum concentration of total ammonia was stated as 500mg litre^{-1} to protect public water supplies. The control of nitrate was not recorded other than substances such as mercuric nitrate where the desire was to control the level of mercury. Interestingly, phosphorous was clearly regarded as the major cause of eutrophication and in Annex 3-1 the goals of phosphorous control were detailed. A target of reducing maximum phosphorous levels to 0.5mg litre^{-1} for municipal waste was stated with unspecified targets for industrial discharges and domestic drainage.

It has already been stated that lakes are far less tolerant of nutrients than rivers and that the recovery process is not rapid. Models have been constructed to predict the effect of various courses of action upon the reversal of the eutrophication process [4]. These

include aeration with oxygen, dredging to remove sludge high in nutrients, removal of hypolimnic water to increase phosphorous retention by sedimentation and of course reduction in nutrient input. From these studies it was concluded that the most effective method to reverse the eutrophication process was to reduce the input of nutrients into the lake. Despite the difficulties in modelling a complex ecosystem, such a conclusion fits well with actual experience. The intentional addition of nutrients to lakes has given a valuable insight into the roles of both phosphorous and nitrogen in the process of algae formation [5]. It has been established that for a number of lakes studied it is the level of phosphorous which regulates the production of algae. Any nitrogen deficiency appeared to be balanced by the fixation of nitrogen via the blue-green algae. The control and regulation of nitrogen nutrients in many lakes would not result in a reduction of blue-green algae. The subsequent eutrophication process would be predicted therefore to continue. However, a reduction in the level of phosphorus nutrients would be expected to have a significant effect on the production of the algae.

Although the prevention of nutrient enrichment of lakes will speed up the reversal of eutrophication it is necessary to have a knowledge of the source of such nutrients. As has already been found, each lake can respond differently and the source of nutrients may vary depending on its location. In the case of Lake Mendota, Madison, Wisconsin, it was found that rural runoff, municipal and industrial waste water accounted for 78% of the phosphorous total [1]. For nitrogen, ground-water and precipitation contributed 72% of the total, with fixation only providing 0.4%. It was speculated that this illustrated a lake whose eutrophication process was regulated by phosphorous input.

The case for an increase in controls on nitrogen based nutrients such as fertilisers has not been proven. Such changes in control would not be expected to result in a reduction in river and lake eutrophication. Phosphorus nutrients on the other hand have been clearly identified as large contributors to the eutrophication process and increased control would be justified to reduce and hopefully reverse river and lake eutrophication.

1.1.2 Nitrate in Drinking Water

In reviewing the subject of nitrate in drinking water it is considered desirable to distinguish between current legislation and scientific fact. At present the maximum nitrate concentrate allowable in drinking water is 50mg NO₃ litre⁻¹ or 11.3mg NO₃-N litre⁻¹ under EEC legislation [6]. Currently, within the UK there is a debate as to whether this value was intended as a maximum level for any water sample or an average value over one year's supply [7]. In certain areas within the UK there are difficulties in consistently meeting this value especially in areas of extensive arable farming. Where arable farming is less intensive, nitrate levels in water typically reach a maximum of only 10mg NO₃ litre⁻¹ which is comfortably within the current EEC legislation. As recently as 1984 the World Health Organisation (WHO) were prepared to specify nitrate levels in drinking water listed up to 100mg NO₃ litre⁻¹ as conditionally acceptable [8]. However, a target of less than 50mg NO₃ litre⁻¹ was recommended. Since then the level has been reduced to 45mg NO₃ litre⁻¹ based on the occurrence of infantile methaemoglobinaemia or blue baby syndrome.

Drinking water provides only part of the dietary intake of nitrate with vegetables, cereal, meat and to a lesser extent dairy products providing the balance. Obviously the

daily nitrate intake of humans varies depending on diet and is noticeably higher for vegetarians. Beetroot, celery, lettuce, radish and spinach have high nitrate levels of greater than 2.5g Kg^{-1} , compared with tomatoes, peas, beans, potatoes and mushrooms which contain one tenth of that level. Milk contains a maximum of $5\text{mg NO}_3 \text{ litre}^{-1}$ and therefore, for bottle fed infants water can be the main source of nitrate. The average dietary nitrate intake for adults varies from $30\text{-}300\text{mg NO}_3 \text{ day}^{-1}$, with the higher intake levels characterised by vegetarians or high nitrate levels in drinking water. For vegetarians with a low nitrate intake from drinking water, 80% of the daily nitrate is from vegetables. The worst case, that of a vegetarian in a high nitrate drinking water area, could theoretically have a nitrate intake significantly in excess of $300\text{mg NO}_3 \text{ day}^{-1}$. In addition, nitrate is synthesised by man and the actual daily amount is difficult to confirm but is of the order of 50mg day^{-1}

1.1.3 Effects in Man

It has been shown that nitrate itself has a relatively low toxicity and therefore concern centres on the conversion products following ingestion. Nitrate is reduced to nitrite by bacteria with nitrate reductase activity [6]. Typically this occurs in the mouth, stomach, intestine and colon. The rate is influenced by the bacteria present, availability of nitrate and pH of the stomach. The nitrite can be converted into urea and amino acids. Concern has recently focused on the carcinogenic N-nitroso compounds formed by the reaction of nitrite with primary amines.

Earliest signs of nitrite toxicity are methaemoglobinaemia together with a reduction in blood pressure [6]. In particular the concern is with infantile methaemoglobinaemia

caused by the reduction of nitrate to nitrite and subsequent conversion of (ferrous) oxyhaemoglobin to (ferric) methaemoglobin. The latter is incapable of transporting oxygen throughout the body and the net result is cyanosis and tissue anoxia. Cyanosis is the characteristic blue colouration of the skin caused by the lack of oxygen and in infants commonly referred to as blue baby syndrome. When between 45% and 65% of the haemoglobin has been converted to methaemoglobin, death will result. Since 1945 there have been around 3,000 cases of blue baby syndrome. There have been some fatalities although the last reported death in the UK was in 1950. The last confirmed case was in 1972 and one characteristic of these cases, was the use of well water with nitrate levels of 100mg litre^{-1} . In addition the well water had often been shown to be of poor quality with the infants suffering from gastro-intestinal upsets. This can cause an increase in the reduction of nitrate to nitrite. There is no evidence to suggest that piped water supplies with nitrate levels up to 100mg litre^{-1} cause methaemoglobinaemia.

The reduction of nitrate to nitrite by bacteria and the subsequent theoretical reaction with primary amines in the human stomach has given rise to concern. N-nitroso compounds have a well documented carcinogenic effect upon a range of animals. Such compounds have not yet been proven to be carcinogenic to humans. Despite the lack of evidence, it is widely considered that for these reasons, the daily nitrate intake should be regulated. This would control the level of nitrate reduction to nitrite and hence limit the potential for formation of N-nitroso compounds in the human stomach.

1.1.4 Effects on Agricultural Practice

The agricultural industry have been clearly identified or "blamed" for the problems of nitrate pollution with emphasis on modern intensive farming practices. Farmers are viewed by the water industry as potentially large polluters and for this reason a code of practice has recently been issued [9]. The possible pollutants include pesticides, sheep dip solution, silage effluent, milk and dairy waste and waste from animal processing. The code focuses on control of slurry pollution, milking parlour washing, silage effluent and surface run off. This accounted for 70% of all farm pollution incidents in 1989, with severe consequences for the affected waterways. Section 13 of the code deals solely with the control of nitrate lost from land. The aim is to achieve improvements at little or no extra cost to the farmer. The main points for effective nitrate leaching control are summarised below:

- 1 Ploughing up grass: Large nitrate releases occur when grassland is ploughed.
- 2 Organic manure: Higher nitrate leaching risk than from inorganic fertilisers. The maximum application rate recommended is 250kg ha⁻¹annum⁻¹.
- 3 Inorganic nitrogen: The application rate for each field should be calculated taking into account crop requirement. MAFF recommendations [10] should be used to establish the economic optimum application rate.

- Fertilisers should not be used in autumn for cereal crops.
- 4 Crop cover: Bare soil over winter months results in significant nitrate leaching. Crops should be sown to ensure growth by early September. Crops growing by mid October will not reduce nitrate leaching.
 - 5 Crop residues: Crop residues should be mixed into the soil ideally just prior to sowing the next crop. This is especially true for high nitrogen containing non cereal and vegetable crops.
 - 6 Autumn Cultivation: The cultivation of land should be delayed for as long as possible without extending the date for sowing the next crop.
 - 7 Managing grassland: The grassland grazing intensity should be reduced especially in the autumn months.
 - 8 Irrigation: Adequate irrigation normally reduces nitrate leaching. (Avoid applying too much on an uneven irrigation pattern).

1.1.5 Nitrate in Drinking Water - Removal

For a number of years it has been common practice to blend waters with a high nitrate level to comply with current legislation. The viability of this option is threatened by the availability of low nitrate water and the cost of pumping over long distances. A number of alternative methods exist for the removal of nitrate from drinking water [11]:

- a. ion exchange (IX);
- b. reverse osmosis (RO);
- c. electro-dialysis (ED);
- d. biological nitrate removal (BNR);
- e. chemist nitrate removal (CNR).

The techniques of IX, RO and ED are well established and have identifiable capital and running costs. The process of biological nitrate removal relies on denitrification using specialised anaerobic micro-organisms. The new CNR method is a combination of electro-dialysis with a roto-bio-reactor (RBR). Fixed bed particulate systems suffer from accumulation of biomass and fermentation gas bubbles. The RBR avoids these problems by a continuous rotating action. Each method is applicable under a narrow set of processing conditions with different capital and running cost requirements. With increasing levels of nitrates in water, a method to reduce nitrate levels will be required. The cost of this operation will ultimately be passed onto the consumer resulting in higher water charges for individual households and industry.

1.2 Standard Analytical Methods for Nitrate Determination

1.2.1 Direct Spectrometric Method

There are numerous spectrometric methods for the quantification of nitrate and the simplest involves the direct determination by ultra violet (UV) spectroscopy. The nitrate anion absorbs strongly in the 210 - 220 nm region and absorbance is usually measured at 210 nm [12]. Dissolved organic matter introduces a significant interferent because of absorption in the same UV region as the nitrate anion. To partially compensate for this an additional measurement at 275 nm is recommended. It is possible to determine the nitrate concentration in up to 10 samples per hour and interferences from carbonate or hydroxyl anions can be tolerated up to a maximum of 2,000mg/l (as CaCO₃) provided the sample is acidified before analysis. Chloride does not interfere with the analysis and nitrite present in the sample to a maximum concentration of 6.4 mg/l can be tolerated by using treatment with sulphamic acid. Turbid samples must be filtered since light scattering by undissolved particles is a major source of error in UV spectroscopy. A detection limit of 0.01 mg/l NO₃-N is achieved with a linear range of up to 2 mg/l NO₃-N.

1.2.2 Colourimetric Methods

Chromotropic acid (4,5-dihydroxy 2, 7-naphthalene disulphonic acid) reacts with nitrate to form a yellow product with a maximum absorption at 410nm which makes it suitable for spectroscopic analysis [13]. The working concentration range is 0.1-5 mg/l NO₃-N. However the method is subject to a number of interferents. Among these nitrite can

be removed by the addition of urea and residual chlorine and oxidants can be removed by the addition of sulphite. Chloride is masked by the addition of antimony as is the interference from the yellow iron(III)chloride [14].

Nitrate can be reduced to nitrite and used to diazotise an aromatic amine which in its turn is coupled to produce a dye. The reduction can be effected by a number of different methods, such as a strongly alkaline (pH 12) solution of hydrazine sulphate with copper sulphate as the catalyst [15]. Alternatively, commercially available cadmium granules treated with copper sulphate may be used to quantitatively reduce nitrate to nitrite [14]. The nitrite is then derivatised by reaction with N-1-naphthylethylene diamine dihydrochloride (N1NED) and sulphanilamide. The reddish-purple dye is then determined spectrometrically at 520nm. The major advantage of this method is that it can readily be automated and forms the basis for commercial autoanalysers. Twenty samples per hour can easily be analysed and a limit of detection of 0.01 mg/l NO₃-N can be achieved. The major interferent is that of particulate contamination which can be removed by filtration or centrifuging the sample.

An automated spectrophotometric field monitor was described by Worsfold, Clinch and Casey [16] who monitored nitrate levels in the River Frome. The equipment was based on flow injection analysis (FIA) by the reduction of nitrate with copperised cadmium and derivatisation by N1NED and sulphanilamide. During a 14 day trial, 2.5 litres of an ammonium chloride carrier stream and 2.5 litres of the colour reagent (N1NED and sulphanilamide) were consumed. The monitor required weekly attendance to replace the cadmium reduction column and replenish the reagent solutions. The limit of

detection was $24\mu\text{g l}^{-1}$ $\text{NO}_3\text{-N}$ and linear up to 12mg l^{-1} $\text{NO}_3\text{-N}$.

The automated methods enable a high sample throughput but consume a large amount of reagents [17]. This adds a high consumable cost to the already significant capital investment required for instrumentation. Automation does minimise actual exposure to toxic materials such as cadmium and N1NED. This can otherwise be a significant problem in a manual method. The biggest single source of poor precision and accuracy is the fouling, or formation of deposits, on the internal surfaces of the analyser. The problem is most pronounced when biota are present in the sample. They are able to multiply rapidly as in the case of surface water samples.

1.2.3 Reduction to Ammonia

Nitrate and nitrite can be determined by the reduction to ammonia using Devarda's alloy which is a mixture of 50% Cu, 45% Al and 5% Zn [18]. The reduction is carried out in a Kjeldahl distillation apparatus and the ammonia produced determined spectroscopically [15]. The spectroscopic determination of the brown coloured reaction product of NH_4^+ and Nessler's reagent, K_2HgI_4 , under alkaline conditions is utilized. Any ammonia present in the initial solution must be removed by boiling under alkaline conditions. Both nitrate and nitrite can be determined simultaneously. The analysis takes 1 hour to perform and is suitable for nitrate in the range 12-40 mg/l $\text{NO}_3\text{-N}$. It is possible to determine the distilled ammonia by either the proposed spectrometric method or by titration.

1.2.4 Chromatographic Methods

Although methods are available for the determination of individual anions, only ion chromatography is able to determine the following with a single method: fluoride, chloride, nitrite, phosphate, bromide, nitrate and sulphate anions. Typically a 100 μ l sample is injected on to the column and eluted with alkaline sodium carbonate eluent. The anions are separated on the ion exchange column according to their affinity for the strongly basic anion exchanger [19]. After separation, the anions are converted to their conductive acid form by a cation exchanger column and measured by means of a conductivity detector. Retention time data for standards is compared to that of samples and quantitative measurements made by means of peak height or peak area. The detection limit for nitrate is typically 0.1 μ g/l NO₃-N. The main interference is from particulates which can block the column and normally a guard column is used. A large excess of any one anion relative to others, such as chloride from sea water can present problems requiring removal of the anion. Certain manufacturer's claim that seven anions can be separated within 6 minutes [20]. For automated analysis, only two samples can be completed each hour. This presents a major obstacle to the adoption of the technique for the continuous determination of nitrate or other anions of interest.

1.2.5 Electrochemical Methods

Cyclic voltammetry at a stationary mercury drop electrode has been used for the determination of nitrate in natural waters. The electro-reduction of nitrate to ammonia and hydroxylamine was catalysed by the trivalent cation lanthanum (III) [21].

Two cyclic voltammograms were recorded in the range -0.8 to -2.0V versus a standard calomel electrode. Sulphate interference was removed by precipitation with the addition of barium chloride. The method used was linear up to 1500 m mol/l NO₃⁻ with a detection limit of 3.4×10^{-6} m mol/l. The large linear range offered a benefit but the relatively high detection limit was a significant disadvantage.

There is a recognised need for an analytical method for the determination of nitrate in water, and the techniques discussed above all suffer from one or more major limitations. Such as interference, cost of equipment, cost per sample, low sample rate, poor detection limit or small linear range. Ion selective electrodes have a unique combination of features and benefits and are the preferred method of analysis of nitrate in water. The instrumentation required is of low cost, robust and portable such that field testing is straightforward. It is possible to construct fully automated equipment with a high sample throughput for industrial applications. The technique measures activities and not concentrations and has a very large linear range. ISEs have some limitations in terms of selectivity, lifetime of membrane material, drift and sensitivity to temperature. These areas provide the opportunity for improvement and enhancement of the role for ISEs.

1.3 Ion Selective Electrodes

1.3.1 Nitrate Determination

Potentiometry is perhaps the best known electrochemical method, and it is possible to reduce nitrate to NH₃ quantitatively using titanium (III) chloride [14]. The final

determination can then be made using a commercially available ammonia gas sensing electrode. This method will determine NO_3^- , NO_2^- and NH_3 . The linear range is 0.1 to 20 mg l^{-1} $\text{NO}_3\text{-N}$ with a sample volume of 50ml and a precision of $\pm 3\%$. The disadvantage of the method is that if either ammonia or nitrite is present in significant amounts it should be determined separately.

The nitrate ion selective electrode (ISE) responds to the activity of nitrate in solution by developing a potential across a thin permselective membrane separating the test and filling solutions. A double junction reference electrode with the outer chamber filled with ammonium sulphate solution completes the electrode cell [22]. In theory the technique offers a unique combination of simple and rapid analysis [23]. In practice it is necessary to add reagents but the simplicity is normally preserved. The simple reliable and cheap equipment lends itself to field determinations. Battery operated portable instruments provide rapid results but without the high precision achieved in laboratory conditions. The technique also lends itself to use in on-line continuous analysers. It is necessary to control carefully the temperature of both standards and samples to within $\pm 0.1^\circ\text{C}$ for high precision work. At low activities, the simplicity and rapid response is sometimes lost because of the time taken to reach equilibrium.

The linear range is between 10^{-5} and 10^{-1}M (0.14 to 1400 mg l^{-1} $\text{NO}_3\text{-N}$) using either a calibration curve or standard addition method. Turbid samples can be determined without pretreatment. Both chloride and bicarbonate are recognised interferents but can be easily removed [24]. Other anions which also cause interference but not normally occurring in potable waters are, NO_2^- , CN^- , Br^- , I^- , ClO_3^- and ClO_4^- . The ionic strength must be held constant by the addition of a buffer. This may contain Ag_2SO_4

to remove halides, sulphamic acid to remove NO_2^- , $\text{Al}_2(\text{SO}_4)_3$ added to complex organic acids and buffered to pH3 to remove HCO_3^- . A precision of $\pm 2.5\%$ is achieved over the concentration range provided a slope of $-57 \pm 3\text{mV}$ is maintained. Recalibration is required a number of times during the day to allow for any electrode drift.

In view of the cost of silver, an alternative ionic strength adjustment buffer (ISAB) has been investigated for nitrate analysis using an ISE [25]. The use of a lead acetate - lead oxide ISAB was evaluated for nitrate analysis in soil and plant extracts and water samples. Reproducible results were produced and validated against those obtained using the standard Ag_2SO_4 buffer, a spectrometric and ion chromatographic method. The new buffer is some 15 times cheaper than the silver based system and less susceptible to variation in cost.

The effects of surfactant interference on the determination of nitrate in stream waters using an ISE was reported [26]. Samples were taken from streams flowing into Lake Biwa, the largest lake in Japan, and intentionally contaminated with an anionic surfactant sodium dodecylbenzenesulphonate (DBS). It was found that the addition of a cationic surfactant, cetyltrimethylammonium bromide (CTMA) removed the interference from DBS by complex formation. This was suitable for a DBS concentration up to 10mg l^{-1} .

Nitrate selective microelectrodes with a tip diameter of $1\mu\text{m}$ can be fabricated using a liquid ion exchanger. Such electrodes can be used to investigate samples where high spatial resolution is required or where the physical size is small such as plant cells. A nitrate selective microelectrode was constructed and found to have a slope of -55 mV

decade⁻¹ with a linear range 10^{-1} to 10^{-5} M [27]. Selectivity coefficients were of the same order as achieved with macro or normal nitrate ISEs. These microelectrodes were used to study the nitrate gradient in freshwater lake sediments where a spatial resolution of greater than 0.5mm was required. The microelectrode was not suitable for the evaluation of seawater sediments because of the interference from chloride.

There is a recognised need for the determination of the activity of ions in a wide variety of sample types. Simple sensors capable of being used in flowing streams and even living cells have been the subject of considerable research. A successful approach to the design of such sensors has been the development of electrodes exhibiting Nernstian potentiometric responses but with selectivity to the ion of interest. The critical feature of these ISEs is the selective membrane which may be a glass, solid or a liquid. The latter offers the greatest versatility, although sometimes compromising the selectivity achieved. This arrangement, however, gives the greatest number of physical problems in maintaining electrical contact between the internal filling solution, the liquid ion exchanger or neutral carrier in solution and test solution. The entanglement of the ion exchanger and latterly neutral carrier within a plasticised poly (vinylchloride) (PVC) matrix has significantly simplified electrode construction since 1970 [28].

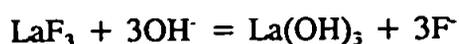
1.3.2 Theory

There are a number of types of ISEs as shown below:

- a) glass membrane electrode;
- b) solid state electrode;
- c) liquid membrane electrode;
- d) gas sensing probes.

The glass electrode, or pH electrode, is probably the best known ISE and has been in standard laboratory use since the 1930's. The electrode functions by an ion exchange process which takes place within the hydrated section of the glass surface [29]. The developed charge is believed to be transferred across the membrane by an ionic interstitial mechanism with each charge carrier moving a few atomic diameters.

Inorganic salts can be pressed into a pellet shape and used as the ion exchange membrane for solid state electrodes. In 1966, Frant and Ross [22] commercialised the fluoride ISE based upon lanthanum fluoride doped with a low level of europium (II) to increase conductivity. The response mechanism is by simple ionic conduction via F⁻ ions. The interference from hydroxyl ions has been shown to be due to the reaction



rather than entry of the ion into the membrane matrix.

It is possible to sub-divide liquid membrane electrodes into those based on neutral carriers and those utilising ion exchangers. The neutral carrier membranes are best exemplified by the well established valinomycin based potassium ISE. This was first described by Stefanac and Simon in a Swiss Patent in 1966 [30]. By 1972 a clinical analyser was available for potassium determination based on the valinomycin containing ISE.

The first example of an ISE based on an ion exchanger was the calcium selective ISE using calcium didecylphosphate in di-n-octylphenyl phosphonate [31]. Moody, Thomas and Oke [28] used the same electroactive components to fabricate the first successful PVC membrane electrode. It was nearly Nernstian in response to calcium. The long

functional lifetime was identified as a positive improvement over liquid membrane electrodes.

Gas sensing probes utilize two membranes, one to allow the gas to diffuse through whilst the other is normally an established ISE membrane with detection by potentiometric response [32]. Probes for the determination of dissolved CO₂ and NH₃ are well established. A standard method for the determination of nitrate by reduction to NH₃ and final determination by the ammonia probe has been reported earlier in section 1.3.1.

In all of the cases above, potentiometric measurement is performed with negligible current flow by the use of a high impedance electronic voltmeter. Typically the reference electrode is the established silver/silver chloride electrode which has a well documented and stable potential. The membrane must be permselective so that the ion of interest is "exchanged" whilst co-ions are excluded [33]. A membrane potential or boundary potential (Donnan potential) is generated at the test solution - membrane interface. The magnitude of the developed potential (E) is dependent on the activity of the counter ion or ion of interest and obeys the Nernst equation shown below. For a singly charged anion, an electrode with a response of -55 - 59.1 mV decade⁻¹ is considered to be Nernstian [22].

$$E = E^{\circ} - \frac{RT}{zF} \ln a$$

E° = standard potential

R = Molar gas constant

T = temperature in Kelvin

z = charge on the ion

F = Faraday constant

a = ion activity

for monovalent anions at 25°C (298K) this simplifies to

$$E = E^{\circ} - 0.059 \log a$$

1.3.3 Development of Nitrate Ion Selective Electrodes

In their first nitrate selective electrode, Orion utilized the Ni(II) phenanthroline complex as the ion exchanger dissolved in p-nitrocymene, a water immiscible solvent [22,34]. Beckman and Corning utilized quaternary ammonium salts as the ion exchanger which had a similar selectivity for nitrate in the presence of a range of common interferents.

The first commercially available nitrate ISEs were based on a porous membrane holding a water immiscible mixture of the electroactive material and a solvent. Such an arrangement lacked mechanical rigidity and electrical contact with the test solution relied on continuous leaking of the solvent into the sample. Variations in pressure and temperature severely affected the test solution/filling solution interface resulting in an erratic response and drift.

In 1970, the classical paper of Moody, Oke and Thomas [28] proposed the use of PVC as a membrane support material for a calcium selective electrode. This simplified membrane fabrication [35] and at the same time overcame the problems associated with

porous plug electrodes. Davies, Moody and Thomas [36], incorporated the active ingredients of the Orion and Coming nitrate selective electrodes into a PVC membrane. It was found that the lifetime of the electrodes were extended. Other properties such as response characteristics and selectivity were not significantly different to that of the porous plug electrodes.

Nielsen and Hansen [37] attributed the poor stability of both the porous plug and PVC membrane electrodes evaluated by Davies *et al* as being due to the high water solubility of the ion exchanger. Solubility parameters were used to select tetradodecylammonium nitrate as the optimum ion exchanger with dibutyl phthalate as the solvent mediator. This gave a Nernstian response and a limit of detection of $8 \times 10^{-7} \text{M NO}_3$. The membrane composition has been successfully utilised in commercially available nitrate selective electrodes. The role of the solvent mediator in polymer membranes is of particular interest and has been investigated for nitrate selective electrodes [38]. The Ni(II) phenanthroline complex was used with the following solvent mediators: 2-nitro-p-cymene (NC), 2-nitrophenyloctyl ether (2-NPOE) and 2-nitrophenylphenyl ether (2-NPPE). Solvent mediators are liquids at room temperature which are believed to have a number of roles within the membrane. It has been claimed that the selectivity of the electrode was influenced by the dielectric constant of the solvent mediator. The other role of solvent mediators is to soften the PVC to produce a rubbery material at room temperature [39]. Compatibility with the PVC is essential to prevent a two phase membrane with freedom from surface exudate. This can often be characterised by a greasy membrane surface. Both 2-NPOE and 2-NPPE were found to give membrane lifetimes in excess of 10 months. The dielectric constants for the solvent mediators were as follows: N.C. 17.7, 2-NPOE 23.5 and 2-NPPE 28.3. Within this range the

different mediators were found to have little effect on selectivity coefficients. The role of solvent mediators as softening agents that are compatible with the PVC have been demonstrated. The case for the importance of dielectric constant affecting properties other than compatibility still requires further investigation. The ion transport both in liquid and membrane nitrate selective ISEs have been studied by Mathis, Stover and Buck [40,41] to gain an understanding of factors necessary to improve new sensors. The study included the following support polymers; cellulose tricetate, PVC-acrylonitrile, polypropylene and polytetrafluoroethane. The solvent mediator used was nitrobenzene with Aliquat 336S (tricaprylmethylammonium nitrate) as the electroactive material. It was shown that Aliquat 336S in nitrobenzene was a weakly associated liquid ion exchanger. Increased loading of the ion exchanger lowers the dielectric constant of the membrane and is predicted to improve selectivity for larger anions. It is expected that this will have a negative effect on the limit of detection by increased dissolution of the ion exchanger. The rate limiting step in the response process was ionic diffusion through the membrane surface layer or slow interfacial kinetics.

A nitrate selective electrode was fabricated [42] by the incorporation of nitron nitrate in 'Araldite' and allowed to dry producing a 0.5 mm thick membrane. The nitrate ISE produced a slope of -50mV decade^{-1} and gave a linear response down to 10^{-4}M nitrate. The electrode only had a lifetime of 6 weeks after which time the response deteriorated. The selectivity coefficient $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ of 2.9×10^{-1} was rather poor and would present a significant limitation on the utilisation of such an electrode.

A liquid ion exchanger electrode was constructed based on the ionic association

of bis(triphenylphosphine)iminium and nitrate anions in nitrobenzene [43]. The electrode gave a fast response with a slope of -58.1 mV per decade at 25°C. The limit of detection was dependent on the ion exchanger concentration which in turn affected the response characteristics. The best detection limit reported was $7.9 \times 10^{-7} \text{M}$. Selectivity coefficients compared favourably with existing liquid membrane and polymeric membrane electrodes for a range of common anionic interferents. However, I^- , SCN^- and ClO_4^- caused considerable interference. The electrode described would still suffer from the disadvantages of liquid membranes such as short term stability and pressure sensitivity.

A study by Mitrakas *et al.* [44] has suggested that the homogeneity of the ion exchanger and PVC affects the response characteristics of the nitrate selective electrode. Superior stability and sensitivity were claimed using quaternary phosphonium salts (QPS) compared to those electrodes based on quaternary ammonium compounds. Optical and electron microscopy analysis showed particles within the PVC-QPS membrane. These were considered proof of inhomogeneity although energy dispersive X-ray analysis (EDXA) was not utilised.

The direct functionalisation of poly(vinylbenzyl chloride) (PVBC) with tri-octylphosphine produced poly(trioctylvinylbenzylphosphoniumchloride) (PTPVBPCI) [45]. After appropriate purification and ion exchange of chloride for nitrate, membranes were solvent cast on a carbon support electrode. The membrane electrode gave a response to nitrate in the range 5×10^{-5} to 0.1 mol dm^{-3} with a slope of $-53.4 \pm 0.5 \text{ mV decade}^{-1}$. Selectivity was similar to that obtained using a conventional PVC matrix and QAS entangled ion exchanger. The $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ value reported was

8.1×10^{-3} with electrode lifetimes of in excess of 10 months but there was a little deterioration in the response.

Recently a nitrate ion sensitive field effect transistor (ISFET) device has been fabricated [46]. The silicon dioxide gate insulator was grafted with 3 chloropropyl dimethylchlorosilane and functionalised with triethylamine to form immobilised quaternary ammonium groups. A slope of only -13mV decade^{-1} was obtained and a combination of poor selectivity and short lifetime will restrict the applications for the nitrate sensitive ISFET device.

1.4 Developments with the Matrix

1.4.1 Poly (Vinylchloride)

There was a strong desire to find an alternative approach to that of liquid membrane electrodes to maintain electrical contact between the test and inner filling solution. In 1967, Shatkay [47] evaluated both paraffin wax and poly(vinylchloride) (PVC) as potential membrane materials. Moody, Oke and Thomas in 1970 [28] reported the first successful PVC polymer membrane electrode. A calcium selective electrode was fabricated by dissolving PVC in tetrahydrofuran (THF) and incorporation of the ion exchanger and solvent mediator. The method was described as solvent casting [35]. This process allowed the volatile organic solvent, THF, to evaporate leaving the polymer membrane with an entangled ion exchanger.

PVC has proved to be an extremely successful polymer matrix. However, there is a

recognised problem of membrane lifetime. This has been shown to be due to both ionophore/ion exchanger and solvent mediator extraction, resulting in loss of electrochemical response [48]. Commercial unplasticised PVC may be regarded as essentially amorphous and has a glass transition temperature (T_g) in the region of 80°C [49]. At the so called 'glass transition temperature' the polymer changes to a glassy material. For PVC, therefore, the introduction of plasticisers or solvent mediators is essential to lower the T_g value and so produce the required rubbery material at room temperature. High levels of plasticisers as typically used in the membrane recipe, can reduce the T_g value to -65°C [39].

The advantages of PVC as the polymer matrix have been summarised as follows:

- (i) high tensile strength;
- (ii) chemical inertness;
- (iii) low T_g value when modified with a solvent mediator;
- (iv) availability;
- (v) low cost;
- (vi) ease of fabrication.

Despite the advantages of PVC, there is a widely recognized need for a polymeric matrix with improved performance. It is interesting to note that PVC is widely regarded as one of the least stable commercially available polymers and would normally require the addition of suitable stabilisers. A recent review by Moody, Saad and Thomas, [50] of membrane matrices showed that around 20 other polymers have been evaluated as alternatives to PVC. The main aim of studies of polymers was to improve membrane lifetime. This can be achieved by either the elimination of the solvent

mediator by selecting a polymer with a T_g value below 25°C (rubbery at room temperature), or by the immobilisation of the ion exchanger and/or solvent mediator. More recently [51], the potential benefits of alternative polymer matrices, particularly those containing functional groups, have been listed as follows:

- (i) possible covalent attachment of water soluble sensors;
- (ii) reduced electrical resistance;
- (iii) improved adhesion to solid substrates;
- (iv) possible attachment of enzymes and other bioreagents for biosensors.

1.4.2 Other Plastics

Plastic materials can be readily defined in terms of the T_g value which is above the room temperature prior to addition of solvent mediators. A number of different plastics have been evaluated as the polymer membrane for potassium selective electrodes. The neutral carrier, valinomycin was used as the electroactive material. Polystyrene (PS) and polymethylmethacrylate (PMMA) were found to be unsuitable polymer matrices [52]. This was because of the high T_g values and poor compatibility with valinomycin and the solvent mediator. From the work, the authors proposed four basic rules for polymer membranes:

- i polymer and electroactive component must dissolve in solvent mediator to give a one phase system;
- ii polymer and solvent mediator should be nonpolar and hydrophobic without electroactive functional groups;
- iii the solvent mediator should dissolve all of the electroactive components,

- be insoluble in water and have a low vapour pressure and high viscosity;
- iv the T_g of the membrane should be well below room temperature.

Recently there has been increasing interest in modifying PVC by the introduction of functional groups such as -COOH and -OH moieties. Buck *et al.* [53], whilst continuing the studies of response characteristics of PVC membranes, evaluated membranes fabricated with a known concentration of PVC-COOH. These groups were considered as fixed ion exchanging sites within the polymer. Nernstian responses were achieved for both potassium and calcium ISEs and an insight into the mechanistic aspects of PVC-COOH and PVC polymeric membranes was described. The PVC-COOH polymer was originally evaluated for better adhesion to substrates and for this reason PTFE plates were utilised for solvent casting. Meyerhoff *et al* [51] found that PVC-COOH without the addition of an electroactive material functioned perfectly as a pH electrode. This could find ready use in medical applications where the extraction of the electroactive material is of concern.

In some clinical applications, potential shifts have been noted due to the influence of proteins on the PVC membrane. This is believed to be due to adsorption rather than extraction at the membrane surface. Simon *et al.* [54] evaluated the use of a higher polarity membrane surface to improve biocompatibility using a hydrolysed poly (vinyl chloride-vinyl acetate) copolymer. The response of potassium, calcium and sodium selective electrodes was evaluated. The response of PVC-OH with 17% hydroxy functionality was comparable to that of the classical PVC membranes. The potential shift was dramatically reduced between aqueous calibration standards and serum samples. PVC-OH was found to have greater adhesive properties which complicated

standard fabrication techniques and the membranes had a lower resistance than the standard PVC electrode.

Poly (vinyl isobutyl ether) was evaluated as a replacement for PVC in the polymer membrane calcium ISE [55]. The best results were obtained with decan-1-*ol* as the solvent mediator. Calcium selective electrodes were fabricated using calcium (bis-di-2-ethylhexyl phosphate) as the electroactive ingredient. The electrodes did not require a conditioning period and gave a rapid Nernstian response with a lifetime less than one month. There appeared to be no specific advantages of poly (vinyl isobutyl ether) as the polymer matrix compared to the already established PVC.

Christian *et al* [56] reported the first ISEs based on an ethylene-vinyl-acetate copolymer (EVA). A calcium sensitive electrode was fabricated using calcium didecyl phosphate in di(*n*-octylphenyl) phosphonate with dioctylphthalate and nitrobenzene as plasticiser. The electrode gave a near Nernstian response to calcium however a susceptibility to static electricity was noted. This could be regulated by controlling the level of 'dryness' of the membrane by limiting the time of air drying. The EVA electrode exhibited superior selectivity to calcium with respect to copper and the alkali metals. The T_g value of EVA is -50°C and it was somewhat surprising, for a polymer which was rubbery at room temperature, that a membrane free from solvent mediator was not reported.

Poly(methyl acrylate) (PMA) was successfully used as the polymer matrix for divalent (water hardness) ISEs based on an ion exchanger and decan-1-*ol* as the solvent mediator [57]. The response was near Nernstian to calcium and magnesium. A reduction in the

level of solvent mediator was necessary to obtain robust membranes free from surface exudate. No specific benefits for PMA were noted compared to the established PVC membrane.

Moody, Saad and Thomas [39] have acknowledged that relatively little is known about the nature of PVC. They evaluated the relationship between relative molecular mass, Tg and calcium electrode response. Electrodes were fabricated from a range of PVC formulations. It was concluded that there were no important differences between the PVC membranes. Polyacrylates were also evaluated but failed to provide a viable calcium electrode. The use of a solvent mediator gave Tg values of -90°C compared with the original Tg value for poly (methyl acetate) of 8°C . Poly (2-methylpropylmethacrylate) did produce functioning electrodes but with poor selectivity.

A nitrate selective electrode based on polyurethane was fabricated by Nielsen and Hansen [37]. This used 80% polymer and diethylphthalate as the solvent mediator. Tetraoctylammonium nitrate was the electroactive ingredient. Response characteristics were similar to those obtained using PVC. The polyurethane membrane did not offer any specific advantages over PVC.

Bachas *et al* [58] evaluated poly(vinylidene chloride) (PVDC) because of its similarity to PVC and the Tg value of the polymer was below room temperature at -17°C . Therefore, a plasticiser or solvent mediator was not necessary to provide a rubbery membrane. PVDC had previously been evaluated by Frend, Moody, Thomas and Birch [59] who found that the use of a solvent mediator produced membranes which lacked

physical strength. Bachas fabricated PVDC membranes incorporating either Aliquat 336 (QAS plus 3-4% m/m octanol and 4-5% m/m decanol) or tridodecylmethylammonium thiocyanate (TDMAT). Membranes based on Aliquat 336 produced functioning electrodes sensitive to thiocyanate with a response of $-56 \text{ mV decade}^{-1}$. Over a seven month period this fell slightly to $-52 \text{ mV decade}^{-1}$. More noticeably there was a reduction in detection limit which was attributed to ion exchanger leaching. The use of TDMAT required the addition of octanol as the solvent mediator however, electrode lifetimes were reduced to only two months, possibly because of solvent mediator leaching.

The use of alternative plastics has improved the performance of polymeric ISEs. To evaluate fully an alternative plastic, it is postulated that the membrane composition should be optimised for that polymer. This would avoid excessive amounts of solvent mediator which can lead to sticky membranes lacking physical strength.

1.4.3 Cross-linked Polymers

Cross-linked silicone rubber has proved successful for use as the polymer matrix for heterogeneous precipitate based electrodes. For this reason, Simon *et al.* in 1973 [60], evaluated silicone rubber as a polymer matrix for potassium selective electrodes. Membranes were cross-linked or vulcanised at room temperature and valinomycin was used as the neutral carrier. A solvent mediator was no longer necessary to produce a functioning electrode and was an advantage in that it overcame the potential problem

of extraction. A Nernstian response was obtained which did not alter after 4 weeks of routine use. Simon *et al.* [61] also reported the successful application of a potassium ISE based on valinomycin and silopren (silicone rubber) for the determination of K^+ in body fluids. A miniaturised electrode was also evaluated. The use of silopren as the polymer matrix almost completely eliminated anion interference in undiluted urine samples. Results for the determination of K^+ in undiluted blood serum showed a good correlation with those obtained using a flame photometer. Correct formulation of the silicone rubber composition was important to provide sufficient physical strength. Simple entrapment of valinomycin within a 3 dimensional silicone rubber structure did not render the electroactive material insoluble but did extend electrode lifetime.

A potassium ISE was successfully fabricated based on a block copolymer [62]. Poly (bisphenol-A-carbonate) and poly (dimethylsiloxane) were used with valinomycin as the neutral carrier. The membranes were claimed to be a two phase system. The poly(siloxane) phase through which charge transfer occurred and the poly(carbonate) blocks formed a crystalline phase that cross-linked the structure. Introduction of 50% of the poly (bisphenol-A-carbonate) polymer raised the dielectric constant from 3.0 to 5.2. This improved the performance of the electrode and the addition of a free solvent mediator was not necessary. The potassium selective electrodes were found to have a stable response after 3 years and a detectable change in response was observed only after 5 years. This may have been due to electrolytic shorting paths through or around the membrane.

The potassium ion selective electrode based on valinomycin commercialised by Philips, first used diphenyl ether as the solvent mediator. Fiedler and Ruzicka [52] were

concerned at this choice because the melting point of diphenyl ether is only 28°C. This can give a problem with so called 'frozen membranes' and the electrode will not respond. Membranes based on PVC, polyurethane (PU) and silicone rubber were successfully fabricated by Fiedler and Ruzicka. The PU and silicone rubber membranes produced electrodes which gave a Nernstian response to potassium. The best results were achieved using PVC with valinomycin and dioctyladipate as the solvent mediator.

A simplified procedure for the fabrication of ISEs has been proposed which eliminates the process of solvent casting [63]. Commercially available polymer tubing was impregnated with the electroactive material by means of a solvent which reversibly swelled the polymer. Evaporation of the solvent returned the tubing to its original dimensions. The electroactive material was entangled in the polymer matrix. Potassium ISEs using valinomycin as the neutral carrier were fabricated with silicone rubber, polyurethane, plasticised PVC and a block copolymer poly(styrene-*b*-ethylene/butylene-styrene) modified with poly(dimethyl siloxane) and mineral oil. All of the polymers gave membranes with Nernstian responses except that of polyurethane where it was suggested that a solvent mediator may be required to improve the response. A pH responsive membrane was fabricated with PVC, and silicone rubber was used as the polymer matrix for the pH, Cl⁻ and NH₄⁺ selective electrodes. None of the polymers evaluated were considered to be superior to that of plasticised PVC. The technique itself offered the opportunity to fabricate electrodes with no visually recognisable membrane area, which could be advantageous in a flow through device utilising specific areas on the tubing. A potassium selective

electrode has been fabricated from silicone tubing and used to study potassium in whole blood [64]. Thin tube sections impregnated with entrapped valinomycin gave the lowest resistance. The silicone rubber showed superior compatibility with blood than the PVC membranes.

Davis and Olejnik [65] used two permselective membranes of Dow Corning Silastic polymer (polymethyl siloxane). An electrode selective toward long chain quaternary ammonium species was successfully fabricated. The two membranes separated the inner filling solution, ion pair solution and test solution. The chosen silastic membranes gave responses which decayed slowly over 24 hours. Such a short lifetime would be expected to limit applications.

Reinhoudt *et al* [66] stated three requirements for a membrane for use with ISFET devices:

- (i) elastomer with T_g well below room temperature, or add plasticiser to achieve a low T_g value;
- (ii) hydrophobic in nature;
- (iii) for cations, the membrane must contain anionic sites or have them introduced by lipophilic anions (eg. tetraphenylborate).

Excellent adhesion to the gate surface was obtained using silopren whereas poly acrylate did not give as encouraging results. The formation of cross-links between the silopren and SiO_2 potassium selective ISFET gate surface was suggested as the reason

for lifetimes in excess of 8 weeks.

Slater [67] reported on the development of a potassium selective ISFET device using alternative polymeric materials. PVC with the associated solvent THF does not lend itself to microscale handling and also absorbs moisture which weakens the ISFET/membrane interface. Butyl methacrylate and a Loctite adhesive were both cured by photoinitiation of the cross-linking reaction. A PVC membrane ISFET can have a lifetime up to 3 weeks, whereas the polymers evaluated by Slater gave ISFET devices with significantly longer lifetimes. The cause of membrane failure was considered to be leaching of the electroactive components as opposed to the breaking of the ISFET/membrane interface.

A photocured polymer on a platinum or copper coated disc was fabricated to act as the sensing electrode for a flow injection analysis detector [68]. The membrane contained entrapped valinomycin and was responsive to potassium. The polymer was an epoxyacrylate and the photoinitiator was benzophenone. Steady state readings confirmed the electrodes gave a Nernstian response to potassium. In the flow injection mode, 70% of the response was achieved in 6 seconds. The electrode behaved in a similar manner to that of a PVC coated wire electrode and offered the specific advantage of rapid fabrication. The high resistance of these membranes was a significant problem and the use of a pin coating technique enabled elimination of the photoinitiator [69]. High energy gamma and electron beam irradiation caused degradation of the valinomycin whilst an ultraviolet laser produced excellent membranes. A platinum disc was spin coated to give a thin film (10 μ m). This was cured in a nitrogen filled chamber by exposure to the ultraviolet (UV) laser for 10

seconds. The electrode response was Nernstian and under flow injection conditions, 80% of the steady state signal was achieved after only 3 seconds. Photoinitiation was thought to lower the membrane dielectric constant. The elimination of benzophenone resulted in improved selectivity coefficients. The membrane showed no observable change in response characteristics after 4 months continuous use.

A calcium ISE has been fabricated using epoxyacrylate and the photoinitiator benzophenone [70]. An alternative polymer to PVC was required because of the time consuming PVC fabrication technique. Solvent casting requires several days for the solvent THF to evaporate. There is little control over membrane thickness or uniformity. Residual quinol stabilisers from the THF can cause erratic responses in coated wire electrodes. The calcium salt of bis[4-(1', 1', 3', 3'-tetramethylbutyl)-phenyl] phosphoric acid was used as the electroactive substance. The membrane was cross-linked using UV light for 40 minutes to initiate the reaction in a nitrogen filled chamber. The membranes were transparent, homogeneous and flexible but had a higher resistance than commercial electrodes. Response was Nernstian in the range 10^{-1} - 10^{-5} M Ca^{2+} , however, at low activities, a stable response was not reached for up to 30 minutes.

A novel use for Urushi, has been evaluated by the fabrication of a polymer matrix perchlorate selective electrode [71]. Urushi a natural oriental lacquer is extensively used for Japanese lacquer ware and contains Urushiol, water, rubbery substances, nitrogen compounds and laccase. It has excellent durability and mechanical strength. For the electrode, tri-n-octylmethylammonium chloride was converted into the

perchlorate form and used as the electroactive substance. Electrodes with a Nernstian response to perchlorate were produced. Selectivity coefficients were similar to commercially available electrodes and lifetimes were found to be in excess of 1000 hours continuous use. An Urushi matrix chloride ISFET device has been fabricated [72]. A quaternary ammonium chloride salt was blended with the Urushi latex and coated on the ISFET gate. Urushi was found to be highly adhesive to the Si_3N_4 substrate. Selectivity of the ISFET device was the same as that for a PVC based device but the Urushi ISFET was responsive for more than two months.

In another approach an insulating film of poly (1,2-diaminobenzene) was formed on a platinum electrode by the electrochemical oxidation of 1,2-diaminobenzene [73]. The polymeric film was insoluble in a range of organic solvents. This supported the suggestion that the polymer was cross-linked via amine linkages. The film was responsive to H^+ over the range pH 4-10. This was believed to be due to protonation of the amine linkages. It was hoped that the technique could be expanded to detect a range of ions working in a similar manner to coated wire electrodes (CWE).

1.4.4 Grafted Polymers

Grafted polymers refer to the modification of the original material by the addition of a functional group as a side chain. This will render the electroactive material insoluble and was expected to improve lifetime and detection limits.

The first work to describe the successful attachment of the electroactive component to the polymeric matrix was reported by Keil, Moody and Thomas in 1977 [74]. A commercially available copolymer, partially hydrolysed poly(vinylchloride-vinylacetate) (VAGH) was reacted with decyl dihydrogen phosphate. The resultant phosphorylated VAGH was then converted to the calcium salt. This together with di(octylphenyl) phosphonate (DOPP) and PVC was used to fabricate calcium selective membranes. These membranes gave electrodes with similar response characteristics to commercially available calcium electrodes based on PVC. A faster response resulted but no other advantages were evident. This electrode was used to determine calcium in the presence of anionic surfactants [59]. The grafted VAGH electrode was compared to a calcium ISE using free calcium (didecyl phosphate) in PVC. The response characteristics including lifetimes were very similar. The VAGH electrode did exhibit poorer selectivity for calcium in the presence of sodium ions.

To improve on the disappointing short lifetimes, the studies were enlarged to include attachment of the solvent mediator to the polymer, [75]. Friedel-Crafts phosphonation of polystyrene did not result in a viable membrane. VAGH grafted with mono octyl phenylphosponate was used together with a little free DOPP to provide functioning electrodes. A slight increase in electrode lifetime was noted with this composition but this was adjudged not to warrant the extra time for membrane fabrication. Interestingly, the combination of immobilising the ion exchanger and solvent mediator using covalent attachment was not included in the study. A reduction in the calcium ion selectivity resulted when the solvent mediator was grafted to the VAGH polymer.

Meares *et al.* [76] evaluated the effect of bonding ion exchange groups to the end of

PVC chains. An amine was used as the chain transfer agent during polymerisation or alternatively, the SO_3^- radical anion was used as an initiator. The electrode was sensitive to anionic and cationic surfactants. Electrode lifetimes were superior to a conventional PVC electrode but the free tricresyl phosphate could be extracted. This occurred after only 6 hours in surfactant solutions and a decline in potential was noted.

Perfluorosulphonate polymer (Nafion) is a commercially available polymer which is chemically inert, hydrophilic, insoluble in water and permselective. Hoyer and Loftager [77] coated a solid state cupric ISE with Nafion to reduce chloride interference. Nafion was coated onto the electrode surface from a ethanol/Nafion solution and then the ethanol was evaporated. Peeling of the coating caused electrode failure and high ionic strength solutions caused visible swelling of the Nafion coating. Freiser and Martin [78] studied Nafion based electrodes by cutting membranes from a film. With appropriate conditioning, either, K^+ , Cs^+ or tetrabutylammonium responsive electrodes were produced. The electrodes showed a high sensitivity for the large organic cations and lifetimes in excess of 6 months were obtained.

Szczepaniak [79] used a mercurated polystyrene as the ion exchanger within either a PVC or polystyrene (PS) matrix to fabricate coated wire electrodes (CWE). The use of PS as the polymer matrix produced mechanically unstable membranes. After appropriate conditioning, Nernstian responses to sodium decyl sulphate (SDS) were obtained. The effect upon membrane lifetime was, perhaps, surprisingly not reported.

Many workers considered that immobilising the electroactive components within the membrane by covalent bonding would give significant benefits. These included,

increased lifetime, faster response, improved detection limits and greater control of stereochemistry leading to improved selectivity coefficients. So far these advantages have not been fully realised despite a large, almost prohibitive, amount of synthetic work.

1.4.5 Covalent Bonding

Ebdon *et al.* [80-85] were the first to combine the recognised benefits of a cross-linked polymeric structure and covalently attached electroactive material. This was achieved without the need for extensive synthetic work. A poly(styrene-*b*-butadiene-styrene) (SBS) block co-polymer was selected as the polymer matrix for the membranes. Both calcium and nitrate selective electrodes have been prepared. The covalent attachment of the electroactive component was combined with the cross-linking reaction. This was possible because of the allyl substituents present in the electroactive material. The cross-linking of the polymer was initiated by the action of heat on a hydroperoxide which generated free radicals. The allyl groups acted as the site of unsaturation and were covalently bonded within the polymeric structure. A proposed reaction mechanism for the covalent attachment of quaternary ammonium salts is shown in Fig. 1-1 and 1-2. [85]. The mechanisms show free radical attack of either the SBS polymer or allyl groups in the QAS. Steric considerations may limit the number of polymer chains which can react with the allyl groups in the QAS.

These SBS electrodes were robust, showed a fast response and extended lifetime but suffered from relatively poor selectivity. This was considered by Moody *et al.* [50] to be due to the omission of solvent mediator from the membrane composition.

Figure 1.1

Route I Radical Attack on Poly(styrene-b-butadiene-styrene)

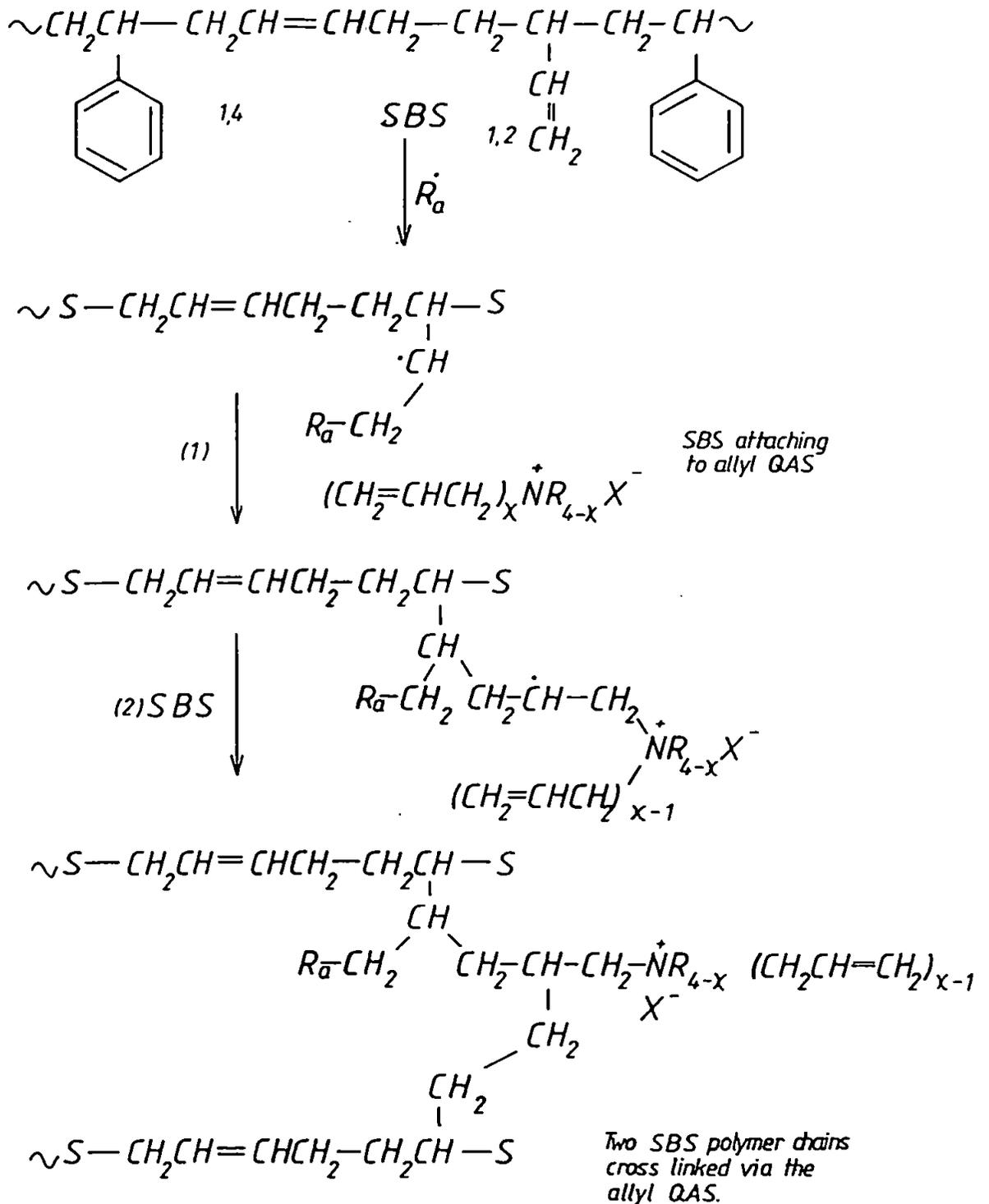
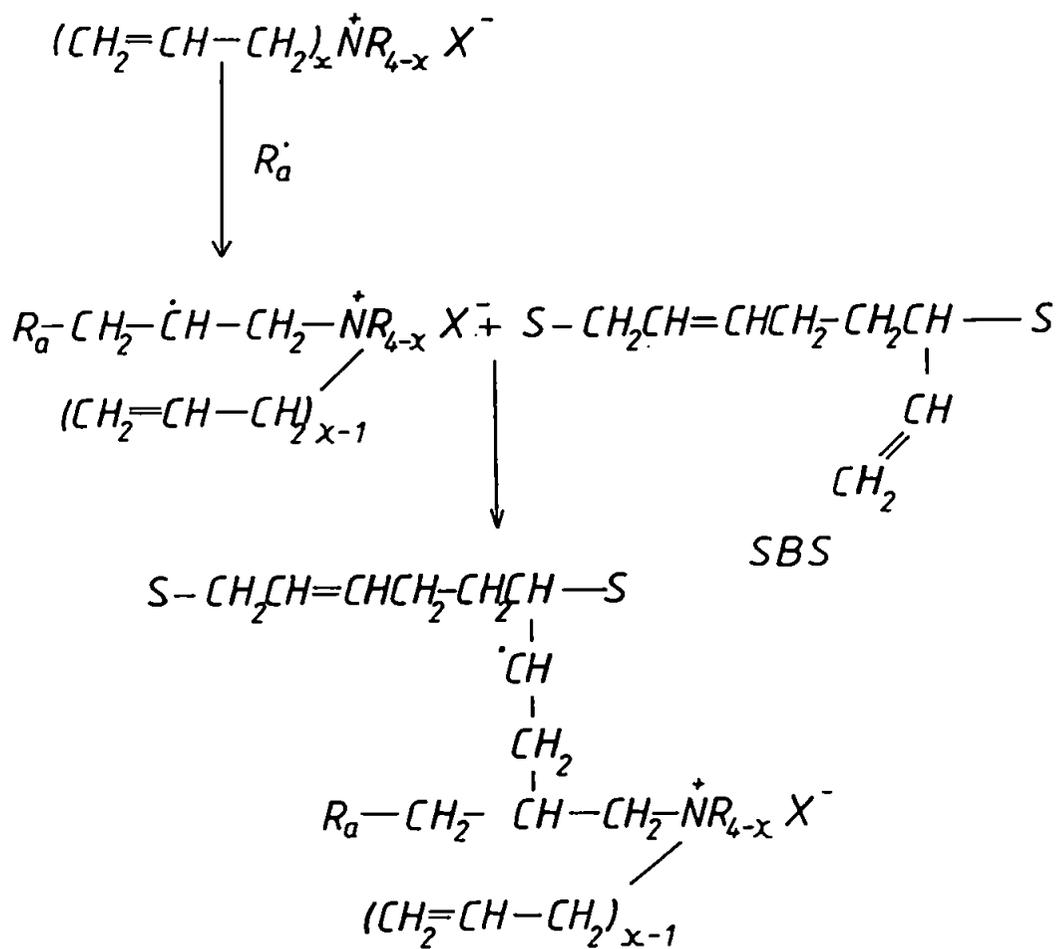


Figure 1.2

Route II Radical Attack on the QAS Allyl Group



Further radical attack will result in cross-link formation either by route I or route II

Calcium selective ISEs were fabricated in three distinct steps [82]:

- (i) cross-linking of SBS with triallyl phosphate plus initiator;
- (ii) alkaline hydrolysis to give a pendant dialkylphosphate;
- (iii) conditioning of the membrane to produce covalently bound calcium dialkylphosphate.

Nitrate selective ISEs were fabricated by the covalent bonding of quaternary ammonium salts to the SBS polymer and subsequent conditioning to produce the quaternary ammonium nitrate salt [85]. The conventional solvent mediators were found to be incompatible with the non-polar SBS polymer resulting in greasy membranes and poor physical strength. The use of a covalently bound mediator for the nitrate ISE did not improve selectivity.

A nitrate selective electrode has been fabricated using crystalline antimonite (V) acid and a polyamide - type epoxy polymer (Araldite) as the polymeric support [86]. The membrane itself contained cross-links and there was some doubt as to the actual electroactive ingredient. Crystalline antimonite (V) acid is a recognised cation exchanger, although tests confirmed that no cation exchange was occurring. The electroactive material may have been quaternary ammonium groups which resulted from the polymerisation or cross-linking reaction of the polyamide. The membranes had a lifetime in excess of 4 months although a slight deterioration in response characteristics was apparent after this period of continuous use.

Ishibashi *et al.* [87] fabricated nitrate, chlorate and perchlorate ISEs, with covalently

bound ion exchange sites within a cross-linked polystyrene. The chloromethylated membrane was quaternarised with, tri-n-octylamine. A range of organic solvents were evaluated and placed in the organic liquid ion exchanger compartment of the electrode body. Appropriate conditioning was used to give electrodes for the ion of interest. A Nernstian response was achieved and selectivities were of a similar order to commercially available electrodes. The limit of detection was poor which was thought to be due to impurities from the fabrication process. Membranes were found to give similar electrode performances after two years storage. The same synthetic approach was used to form chloride ISEs with the membranes soaked in dodecylbenzenesulphonic acid to introduce the sulphonic acid group [88]. It was suggested that the quaternary ammonium group would respond to chloride ions whilst the sulphonic acid group might obstruct interfering ions. This was confirmed experimentally, although excessive sulphonic acid groups resulted in increased interference from cations by affecting the permselectivity of the membrane. In clinical use, deposition of substances from whole blood resulted in an electrode lifetime between 24 and 48 hours.

PVC membranes containing valinomycin and a photopolymerised solvent mediator have been used to form potassium selective ISFET devices [89]. The solvent mediator dihexenyl adipate (DHA) was cross-linked using azo-bis(isobutyronitrile) (AIBN) as the initiator. It was found that extensive cross-linking of DHA was undesirable and only 1.5% conversion gave a 3 to 5 fold improvement in the lifetime. This may have been due to surface cross-linking reducing extraction of the electroactive components from the PVC.

1.5 Aims of this Work

In this study we intend to develop further the novel method for the immobilisation of the electroactive component within a 3 dimensional polymer network reported by Ebdon *et al.* [80-85]. The aim was to develop a nitrate selective polymeric electrode incorporating covalently bound electroactive components. A variety of polymers, solvent mediators and ion exchangers would be used and the fabrication technique improved. Such an electrode should display extended lifetime, improved detection limits, fast response, good selectivity and excellent mechanical strength. Studies will be undertaken in order to understand the mechanism of response and identify the contributing factors to enable the electrode characteristics to be optimised. In future work this would be applied to other ISEs of particular interest.

CHAPTER 2
EXPERIMENTAL

2.1 Polymeric Materials

A range of polymers were evaluated as a potential matrix for ISEs either with covalently bound ion exchangers or, in certain cases, with entrapped electroactive components.

2.1.1 Purification of the Polymer

Analytical-reagent grade chemicals were used unless otherwise stated. Tetrahydrofuran (THF) (BDH, Poole, Dorset, UK) was refluxed over potassium metal (Aldrich, Gillingham, Dorset, UK) and freshly distilled prior to use. This was performed to remove the quinol stabiliser added to prevent formation of unstable peroxides on standing.

Each polymer was purified by dissolving 15g in 75ml THF and reprecipitating the polymer using 200ml cold methanol (Spectrosol grade BDH) unless otherwise stated. The polymer was then collected by filtration and kept under vacuum at room temperature to remove residual solvent. This could take up to a number of days, depending on the permeability of the individual polymer.

2.2 Polymers Evaluated

2.2.1 Poly (Styrene-b-butadiene-styrene) (SBS)

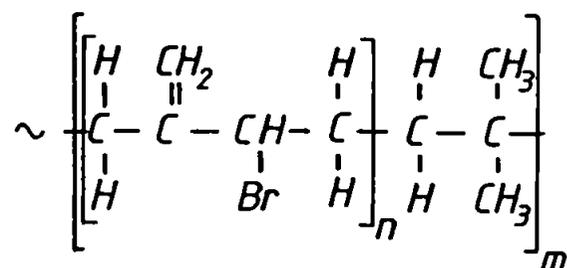
SBS is a block copolymer of styrene and butadiene which is polymerised using anionic polymerisation [90]. The method produces polymers with a controlled molecular weight distribution and a relatively low level of impurities. Of the two SBS polymers TR1101 and TR1102 (Shell Chemicals, London, UK) used by King [85], TR1102 was selected for this work. TR1102 contained 28% styrene with a Shore A hardness of 70 degrees and was chosen because of the higher butadiene content [91]. The cross-linking and covalent attachment of the QAS was predicted to take place within the butadiene block as shown in section 1.4.5 figs. 1.1 and 1.2.

2.2.2 Brominated Poly (Isobutylene-isoprene)

Brominated poly(isobutylene-isoprene), commonly known as bromobutyl rubber, is a copolymer of isoprene and isobutylene. A low level, of isoprene is used to introduce sites of unsaturation to enable cross-linking to take place. The unsaturation is typically around 1 mol % [92]. A solution of the two monomers is cooled in methyl chloride to -100°C. This is then fed continuously into a reactor with a solution of aluminium chloride. Halogenation is performed by treatment of a solution of poly(isobutylene-isoprene) at room temperature with the free halogen. A lubricant, calcium stearate is added together with an antioxidant butylated hydroxy toluene and stabiliser epoxidised soya bean oil. The introduction of chlorine or bromine resulted in various allylic halide structures. The allylic halide increases the reactivity of the unsaturated sites. The structure of bromobutyl rubber is shown in fig. 2.1:

Figure 2.1

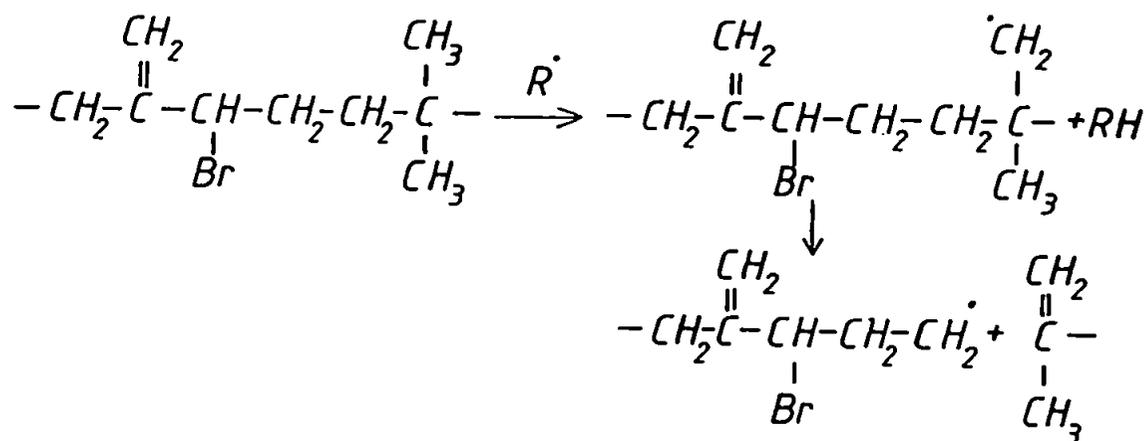
Bromobutyl Rubber



As chain scission takes place by a free radical mechanism shown in fig. 2.2 cross-linking by organic peroxides is not recommended [93]. It is possible to use an organic peroxide to vulcanise bromobutyl rubber provided that a so called 'co-agent' is used. The covalent attachment of the QAS using an organic peroxide initiator was not attempted with bromobutyl rubber.

Figure 2.2

Scission Reaction in Bromobutyl Rubber



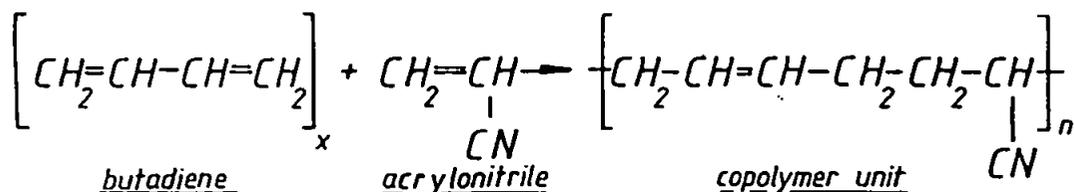
Bromobutyl rubber was purified by soxhlet extraction for 48 hours using acetone followed by removal of residual solvent by storage in a vacuum desiccator. The cross-linked polymer had the advantage of excellent temperature stability up to 120°C for continuous use, good resistance to oxidation from atmospheric oxygen and high mechanical strength. The low level of unsaturation which is predominantly on the side chains as shown in fig. 2.1 accounts for the oxidation resistance. Unfortunately, this essentially non-polar polymer was found to be incompatible with the plasticisers typically used with PVC.

2.2.3 Poly (Acrylonitrile-butadiene) (NBr)

Poly (acrylonitrile-butadiene) is commonly referred to as nitrile rubber and is a random copolymer of acrylonitrile (ACN) and butadiene. The polymerisation is carried out in an emulsion at between 5 and 30°C and the process is referred to as "cold polymerisation" [94]. The butadiene provides both the unsaturation and the rubbery properties of the polymer whilst acrylonitrile is polar and plastic in nature. The proportions of each monomer can be adjusted and commercial grades in the range 18 - 50% ACN are readily available. Krynac 50.75, Krynac 34.80 and Krynac 19.65 (Polysar UK, Guildford, Surrey, UK) with 50, 34 and 19% ACN content respectively were used. The butadiene is present in the trans 1,4- cis 1,4- and 1,2- units typically in the proportion of 77.5, 12.5 and 10% respectively. The structure of NBr is shown in fig. 2.3 and it is expected that cross-linking and covalent attachment of the unsaturated QAS would proceed as shown in section 1.4.5 figs. 1.1 and 1.2.

Figure 2.3

Nitrile rubber showing 1,4 addition



Nitrile rubber was selected in the expectation that the polar acrylonitrile (ACN) content would enable the use of the polar solvent mediators. The unsaturation in the butadiene would enable the use of the novel free radical based immobilisation technique developed by Ebdon *et al* [80-85]. When cross-linked, nitrile rubber gives vulcanisates which are mechanically strong with good resistance to oxidation. The polymer is also resistant to swelling by oils greases and liquid fuels.

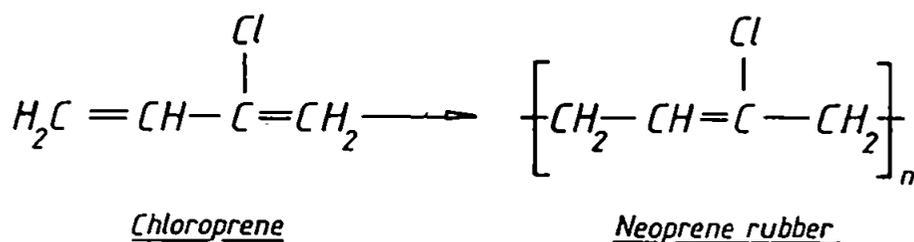
A carboxylated nitrile rubber Krynac 221 (Polysar UK) was also evaluated. This was included because of the success reported by Buck *et al* [53] who evaluated carboxylated PVC. Recent developments by the polymer manufacturers have resulted in a hydrogenated nitrile rubber to give improved high temperature resistance. Such polymers have a controlled level of unsaturation and for Tornac A3855 (Polysar UK) this was 0.5 mol% [95].

2.2.4 Poly (Chloroprene) - Neoprene Rubber

Neoprene was the first oil resistant synthetic rubber to be commercially available. It offers the advantage of compatibility with the polar solvent mediators. Because of the use of emulsion polymerisation, there is a relatively high level of non-rubber constituents in the polymer. Materials such as sulphur and 2-mercapto benzthiazole are added as chain terminators [96]. These residues may affect the electrode response characteristics. The polymer structure is shown below in fig. 2.4 and is present in the trans 1,4- cis 1,4- and 1,2- and 3,4- units typically in the proportion of 90.0, 7.5, 1.5 and 1.0% respectively;

Figure 2.4

Neoprene Rubber 1,4- addition



2.2.5 Poly (Styrene-acrylonitrile) (SAN)

SAN is a random copolymer of styrene and acrylonitrile and is a hard plastic since it does not contain any rubbery portion. The polymer is compatible with the conventional solvent mediators and like PVC would require their addition to form a rubbery polymer

at room temperature. The SAN grade evaluated was Lustran 32 (Monsanto Basingstoke, UK) [97].

2.2.6 Poly (Acrylonitrile-butadiene-styrene) ABS

ABS is a random terpolymer which although containing a low level of rubbery butadiene is a hard and brittle plastic at room temperature. The polymer is compatible with conventional solvent mediators. The butadiene within the polymer enabled the free radical immobilisation technique to be used. The ABS grade evaluated was QE 1083 Natural (Monsanto UK.) [98].

2.3 Organic Synthesis

2.3.1 Introduction

King [85] had found that quaternary ammonium salts (QAS) with allyl substituents could be covalently bound to a SBS polymer network. Triallylethylammonium bromide (TAEAB) and triallylbutylammonium bromide (TABAB) when used as the added ion exchanger gave membranes with the best electrode properties. The QASs were of high purity to minimise potential interference of the electrode response.

Butler *et al* published a series of papers over a ten year period [99, 107] covering the synthesis and polymerisation of quaternary ammonium salts. The synthetic method involved the reaction of unsaturated tertiary amines with allyl halide to yield the QAS. Attempts to polymerise the QASs with benzoyl peroxide and di-*t*-butyl peroxide were

unsuccessful. Tertiary-butyl hydroperoxide (TBHP) was found to give the polymer of the QAS [99]. The compounds reported included, TAEAB, TABAB and triallylbenzyl ammonium bromide (TABzAB).

QASs containing three or more allyl substituents on polymerisation yield water insoluble polymers presumably because a 3-dimensional network can be built up. Water soluble polymers were formed when less than 3 unsaturated substituents were used although all polymers were brittle and had poor physical strength [100].

2.3.2 Preparation of Tertiary Amines - Diallylethylamine and Diallylbutylamine

Diallylamine (Aldrich) (25g 0.257 mole) was placed in a 3 necked round bottom flask and distilled water (25cm³) was added. The mixture was stirred and bromoethane (Aldrich) (28g 0.257 mole) or bromobutane (Aldrich) (35.2g 0.257 mole) as appropriate was added dropwise. Sodium hydroxide solution (May and Baker, Dagenham, UK,) (10.3g 0.257 mole in 25cm³) was added dropwise and the mixture refluxed for a period of 4 hours. The reaction was then cooled and extracted twice with diethylether (BDH, GPR) (50cm³). The diethyl ether extracts were reunited and dried over anhydrous sodium sulphate. After filtration the diethyl ether was then evaporated using a rotary evaporator. The product was distilled under reduced pressure and various fractions were examined by infrared spectrometry (IR). Boiling points at atmospheric pressure were determined for each of the tertiary amines and compared to the literature values. Diallylethylamine as prepared 130°C, literature value [85] 130°C. Diallylbutylamine as prepared 170°C, literature value [99] 170°C. Infrared spectra were recorded using the thin film method for diallylethylamine and diallylbutylamine. The major IR peaks

observed were; =C-H stretch 3080 cm^{-1} (allylic hydrogen), C=C stretch 1640 cm^{-1} (allyl group). No peaks due to N-H vibrations were observed.

2.3.3 Quaternisation Reaction - Triallylethylammonium Bromide and Triallylbutyl ammonium Bromide

Redistilled allyl bromide (4.84g 0.040 moles) (Aldrich) was added dropwise to a stirred solution of either diallylethylamine (4.63g 0.040 moles) or diallylbutylamine (6.1g 0.040 moles) in dried, redistilled acetone (5cm^3). The reaction mixture was cooled in an ice bath and protected from moisture by the use of a calcium chloride guard tube. A white precipitate was seen to develop after 10 minutes and the reaction mixture was then stoppered and cooled in a refrigerator. The product was recrystallised from a 90:10 mixture of redistilled acetone/ethanol.

Melting points were determined for each of the quaternary ammonium compounds and compared to the literature values. Triallylethylammonium bromide as prepared 160°C , literature value [99] 159°C . Triallylbutylammonium bromide as prepared 177°C literature value [99] 175°C . Infrared spectra were recorded using the potassium bromide (KBr) disc method. The major peaks observed were; =C-H stretch 3080 cm^{-1} (allylic hydrogen) and C=C stretch 1640 cm^{-1} (allyl group).

2.4 Synthesis of QASs with longer Alkyl Chain Substituents

The standard QASs used for nitrate ISEs have alkyl substituents up to 12 carbons [22]. King [85] attempted unsuccessfully to synthesise longer alkyl chain tertiary amines

containing allyl substituents. Vizgert *et al* [108] had successfully synthesised an unsaturated tertiary amine with a hexyl substituent by alkylation of the appropriate aliphatic amine with alkenylsulfonates.

2.4.1 Synthesis of Diallyloctylamine

The conditions outlined in Section 2.3.2 did not yield the required product and it was found necessary to modify those parameters. Diallylamine (25g 0.257 mole) was treated with a 2.5 molar excess of bromo octane (124.6g 0.645 mole) (Aldrich) under the conditions described in section 2.3.2. The reaction mixture was treated with 2M hydrochloric acid (130ml) and extracted with diethyl ether (100ml). The diethyl ether layer was removed and the aqueous phase neutralised with aqueous sodium hydroxide to form a turbid solution and a red-orange oily liquid. The mixture was extracted with two portions of diethyl ether (70ml and 50ml) and dried over anhydrous sodium sulphate. The diethyl ether was removed by rotary evaporation to leave a red brown liquid. Analysis both by IR spectroscopy and by gas chromatography (GC) confirmed about 70% purity and the product was further purified by repeating the above procedure. A Sigma 3B gas chromatograph (Perkin Elmer Ltd. Beaconsfield, UK.) was fitted with a 6 feet packed OV101 glass column. The oven was set at 50°C with a ramp rate of 5°C/minute and final oven temperature of 200°C held for 10 minutes. The flame ionisation detector (FID) was set at 300°C and the injection port held at 200°C. After re-purification the product was found to be 95% pure and distilled under reduced pressure. The fraction boiling point 66°C/0.2mm Hg was collected. Identification was

confirmed by mass spectrometry (MS) and elemental analysis (Butterworth Laboratories Ltd.). Found C 80.42%, H 13.23% and N 7.01%, $C_{14}H_{27}N$ required C 80.38%, H 12.92% and N 6.70%. Major peaks from MS were m/z 209, (molecular ion), 110 (100%) ($CH_2=\dot{N}-(CH_2-CH-CH_2)$) and 41 (38.2%) ($\dot{C}H_2-CH-CH_2$)

2.4.2 Synthesis of Diallyldodecylamine

For the synthesis of diallyldodecylamine, the equimolar conditions as described in Section 2.3.2 were used with the reflux period extended from 4 hours to a total of 32 hours over 4 days. Purification was carried out as previously described followed by distillation under reduced pressure. The fraction boiling point $108^\circ\text{C}/0.1\text{mm Hg}$ was collected. Examination by IR and GC found 99.5% purity. Identification was confirmed by mass spectrometry and elemental analysis (Butterworth Laboratories Ltd.). Found C 81.45%, H 13.48% and N 5.57% $C_{18}H_{35}N$, required C 81.51%, H 13.21% and N 5.28%. Major peaks from MS were m/z 265 (molecular ion), 110 (100%) ($CH_2=\dot{N}-(CH_2-CH-CH_2)$) and 41 (21.8%) ($\dot{C}H_2-CH-CH_2$)

2.4.3 Quaternisation of Triallyloctylammonium Bromide and Triallyldodecylammonium Bromide

The reaction as described in 2.3.3 was modified with the replacement of acetone by dry methanol (Spectrosol, BDH) to ensure a lower water content in the solvent. The appropriate tertiary amine was reacted with allyl bromide. The methanol was removed

by rotary evaporation after storage for one week in a refrigerator. The octyl derivative formed a waxy residue which was redissolved in methanol (1ml). Diethyl ether (sodium dried) (20ml) was added and an oil was formed. The supernatant layer was removed and the oil was evacuated at room temperature and a pressure of 0.1mm Hg. A white solid formed which was found to be very hygroscopic and the melting point could not be determined. Identification was confirmed by elemental analysis (Butterworth Laboratories Ltd.). Found C 61.61%, H 10.06% and N 4.45%, $C_{17}H_{32}NBr$ required C 61.82%, H 9.70% and N 4.24%. The presence of bromide ions was established using a standard aqueous silver nitrate test.

The same procedure was carried out for the dodecyl derivative, however, even after repeated purification steps, the product remained a highly viscous and hygroscopic oil. Identification was confirmed by elemental analysis (Butterworth Laboratories Ltd.). Found C 64.01%, H 10.62% and N 3.85%, $C_{21}H_{40}NBr$ required C 65.30%, H 10.40% and N 3.60%. The presence of bromide ions was again established using a standard aqueous silver nitrate test.

2.5 Synthesis of Additional Tertiary Amines and Quaternary Ammonium Salts

The procedures outlined in Section 2.4.2 and 2.4.3 were used to synthesise further tertiary amines and quaternary ammonium compounds. The compounds synthesised are shown in Table 2.1.

Table 2.1

Additional Tertiary Amines and Quaternary Ammonium Compounds

Tertiary Amine	Reacted With	QAS	Melting Point/°C
diallylbenzylamine	allyl bromide	triallylbenzylammonium bromide	131 (132) [99]
tripropylamine	benzyl bromide	tripropylbenzylammonium bromide	181

Identification was confirmed by elemental analysis (Butterworth Laboratories Ltd.).

Triallylbenzylammonium bromide (TABzAB) found C 62.25%, H 7.41% and N 4.58%, $C_{16}H_{22}NBr$ required C 62.3%, H 7.2% and N 4.5%. The presence of bromide ions was established using a standard aqueous silver nitrate test.

Tripropylbenzylammonium bromide (TPBzAB) found C 60.97%, H 9.29% and N 4.37%, $C_{16}H_{28}NBr$ required C 61.2%, H 8.9% and N 4.4%.

2.6 Membrane Materials

2.6.1 Cross-linking

The polymer predominantly used in this work was the copolymer poly (acrylonitrile-butadiene) (NBr) which enabled cross-linking of the polymer chains. The unsaturation in the butadiene was used to covalently bond the quaternary ammonium compounds which contained allyl substituents as shown in section 1.4.5. In previous work tert.-butylhydroperoxide (TBHP) (70% aqueous solution) (Aldrich) was used [80-85] as the free radical initiator and also successfully used by Butler [99] to polymerise

QASs. In the present work TBHP was utilised for the solvent casting technique, but it was considered that a conventional organic peroxide would be more suitable for hot pressed membrane fabrication. Dicumyl peroxide (DCP) (laboratory-reagent grade BDH) was used as received and had the added benefit of eliminating water from the membrane preparation medium.

2.6.2 Solvent Mediators

As discussed in 1.4.1, solvent mediators are essential when PVC is used as the polymer matrix to create a soft and rubbery membrane at room temperature. Since the SBS and NBr polymers are intrinsically rubbery in nature, the use of a solvent mediator did not seem essential. However, some authors [50] believe that the absence of a mediator may result in poor selectivity. SBS was incompatible with solvent mediators which resulted in greasy membranes with poor physical properties [85]. NBr polymer membranes were predicted to be compatible with a range of solvent mediators.

A range of solvent mediators was obtained, *viz*: chlorobenzene (BDH), decan-1-ol (laboratory reagent grade, BDH), di-n-butyl phthalate (DBP) (general purpose reagent, BDH) and 2-nitrophenyloctyl ether (2-NPOE) (selectophore, Fluka, Glossop, Derbyshire, UK) and were used as received.

These materials have been used in a number of applications both as the solvent mediator for liquid anion exchange electrodes and with polymeric membrane electrodes.

2.7 Membrane Fabrication

2.7.1 Solvent Casting

The technique described by Craggs, Moody and Thomas [35] referred to as solvent casting was slightly modified to fabricate cross-linked membranes. The purified polymer (0.53g) was dissolved in freshly distilled and purified THF (6ml), organic peroxide and QAS added with methanol (Spectrosol) (BDH) and solvent mediator if included.

The mixture was then shaken to redissolve any polymer that had precipitated on the addition of methanol and to dissolve the QAS and peroxide. The solution was then poured into a 35mm diameter glass ring on a cellophane covered glass plate. The plate was placed in an oven held at $60 \pm 2^{\circ}\text{C}$ for 6 hours both to volatilise the solvent and initiate the cross-linking reaction.

2.7.2 Hot Pressed Membranes

With the view of improving the control over the membrane fabrication conditions, hot pressed membranes were produced. The mixture was prepared exactly as for solvent cast membranes except that the cellophane was replaced by a polyethylene terephthalate (PET), biaxially orientated film (Melanex film, ICI Films Division, Dumfries, UK). The oven temperature was reduced to 30°C and the membranes subsequently held at reduced pressure in a desiccator to remove any traces of THF or methanol. The membrane was at that stage un-cross-linked and could be physically shaped into a ball

by gentle scraping with a spatula. The material was then placed between two Melanex sheets and compressed in a mould at $150^{\circ}\text{C} \pm 3^{\circ}\text{C}$ for 10 minutes. A pressure of 15 tons was used on a 5" diameter ram in a purpose built hydraulic press (E1180, George Moore Ltd, Birmingham, England) with electrically heated platens. The pressure was applied gradually over a 30-second period to gently force the material into the shape of the former and at the same time expel any air pockets. The mould was custom built (Schiemann Tools Ltd, Bodmin, England) comprising two flat steel plates and the separate former had a diameter of 42mm and was 0.128mm thick. After repeated use, cleaning of the mould and former was performed using a shot blasting machine with glass bead as the abrasive. It was found necessary to remove all traces of solvent from the un-cross-linked membrane prior to hot pressing. Otherwise this might lead to small bubbles forming within the membrane during the heating step of the hot pressing process.

2.8 Electroanalytical Determination

2.8.1 Electrode Arrangement

Discs 7mm in diameter were punched from the master membrane using a hammer and specially made hollow punch similar, to a cork borer. Because the electroactive quaternary ammonium compound was in the bromide form, the membranes needed to be appropriately conditioned. For nitrate selective electrodes it was necessary to condition the membrane in 0.1M potassium nitrate solution (BDH). Membranes fabricated with the SBS polymer could be conditioned in 24 hours, however, it was found that NBr matrix membranes required a period of 7 days for conditioning.

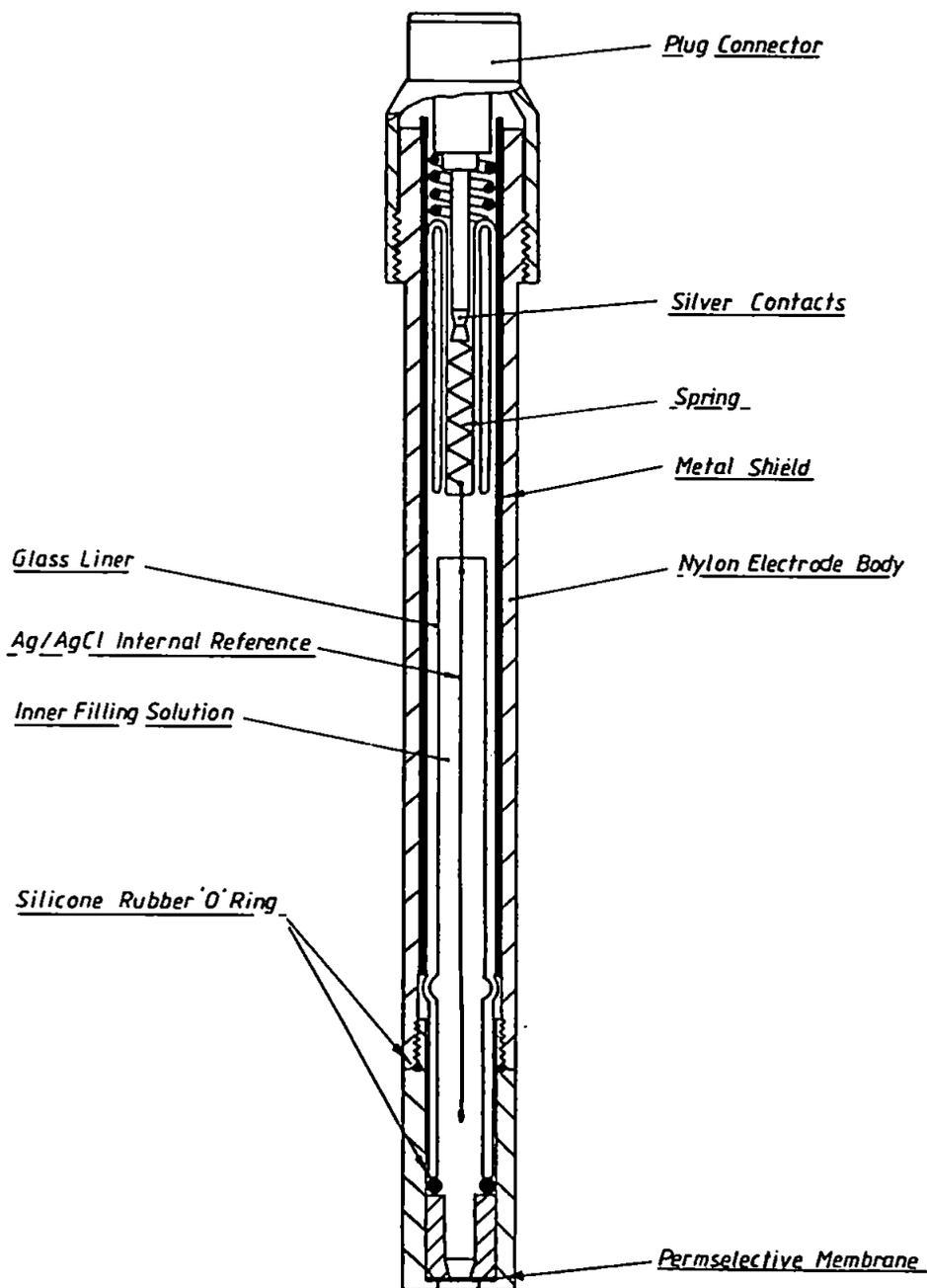
The conditioned discs were assembled in a commercial electrode body (IS 560, Philips Analytical, York Street, Cambridge, UK) and held in place by the detachable tip on to the main body of the electrode. The inner filling solution was a 0.1M potassium nitrate - 0.1M potassium chloride solution (1+1). The full arrangement of the sensing electrode is shown in Fig. 2.5.

2.8.2 Reference Electrode

For nitrate selective electrodes it is recommended that a double junction reference electrode is used to avoid introducing interferences into the test solution. A double junction reference electrode (model 90-02, Orion Research Inc, Cambridge, USA) with a ground sleeve junction was selected. The inner filling solution was a proprietary solution and electrical contact was made with the outer filling solution 0.04M ammonium sulphate (BDH), via a porous plug. The ground sleeve junction provided the electrical contact between the outer filling solution and test solution.

Figure 2.5

Sensing Electrode Arrangement



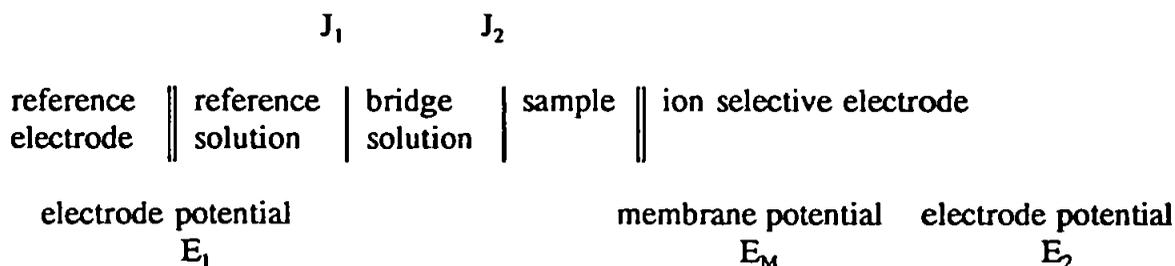
2.8.3 Electrode Measurements

Measurements of electromotive force (EMF) of the complete cell comprising the sensing electrode and reference electrode were made using a digital voltmeter (PW9409 Philips Analytical). The solutions were held at $25 \pm 0.5^\circ\text{C}$ and stirred magnetically. This was achieved using a circulating water bath with a flow return pipe connected to a purpose built stainless steel (grade 316) water bath. Test solutions were held in the water bath both before and during measurement.

Standard solutions were prepared daily using distilled water (AnalaR BDH) and potassium nitrate (AnalaR grade, BDH) with potassium dihydrogen phosphate (AnalaR BDH) at a constant level of 0.01M. Measurements were made by recording the potential for the most dilute standard first and wiping the electrode with tissue before progressing to the next standard. For dilute standards, the response was allowed to stabilise for 5 minutes whilst for other standards a steady potential was reached within 2 minutes. The potential was recorded every 15 seconds to give data on the speed of response.

2.8.4 The Nernst Equation

The electrode arrangement outlined above can be depicted as follows:



J_1 and J_2 denote liquid junction potentials which arise at the interface between two electrolyte solutions that differ in composition or ion concentrations.

The membrane potential results from the exchange of the analyte or counter ion at the membrane surface creating what is termed the Donnan Potential. Such a membrane will exclude co ions and is referred to as permselective.

The cell potential can be shown to be as follows:

$$E_{\text{cell}} = E_1 + E_{J1} + E_{J2} + E_M - E_2$$

If we make the assumption that the potentials E_1 , E_{J1} , E_{J2} and E_2 remain constant then measurement of E_{cell} will enable the membrane potential to be related to ion activity in the sample. It should be stated that liquid junction potentials will vary with change in ionic strength. An ionic strength adjustment buffer (ISAB) is recommended to provide a constant for E_{J2} .

The electrode cell potential can therefore be related to activity of the analyte using the Nernst equation:

$$E = E^\circ \pm \frac{2.303 RT}{zF} \log a$$

E° = cell potential

E = standard potential of the electrode

R = molar gas constant

T = temperature in Kelvin

z = sign and charge on ion

F = Faraday constant

a = activity of ion

At a constant temperature of 298K and for a monovalent anion this reduces to:

$$E = E^{\circ} - 59.12 \log a$$

and for a plot of E against log a, a slope of -59.12mV decade⁻¹ change of a should be Nernstian. It is widely reported that for monovalent anions, a slope not less than -55mV decade⁻¹ is regarded as a Nernstian response and that same criteria has been adopted here.

2.8.5 Activity

In many analytical techniques it is the concentration of the analyte which is determined whereas ISEs respond to the activity of an ion in solution. Activity (a) is related to concentration (c) by the activity co-efficient γ by the equation $a = \gamma c$ and in dilute solutions $\gamma \rightarrow 1$ as $a \rightarrow c$. The Debye-Hückel theory enables mean activity coefficients to be calculated by the equation:

$$\log \gamma = -Az^2 I^{1/2}$$

A = a constant dependent on temperature and the solvent which for water is 0.511 at 298K;

z = charges on the ion;

I = ionic strength where $I = \frac{1}{2} \sum c_i z_i^2$;

c = conc_i, in mol.l⁻¹.

The Debye-Hückel limiting law was derived from electrostatic and statistical considerations of an ion in its environment. At high ionic strengths significant deviations from the law are observed and empirical modifications have been proposed. The extended Debye-Hückel equation used throughout this work to calculate values was:

$$\log \gamma = -Az^2 \left[\frac{I^{1/2}}{1+I^{1/2}} - 0.2I \right]$$

2.8.6 Selectivity Coefficients

One of the important parameters for an ISE is the selectivity coefficient. This is a measure of the response to the primary or analyte ion in the presence of an interfering ion. Unfortunately, the term selectivity coefficient is misleading. The values are not constant since they vary depending upon activity and the method of determination. The selectivity coefficient is defined by the potentiometric selectivity co-efficient, $K_{A,B}^{\text{pot}}$ where ion A is the analyte and ion B is the interferent in the equation below:

$$E = E^\circ \pm \frac{2.303RT}{z_A F} \log_{10} (a_A + K_{A,B}^{\text{pot}} a_B^{z_A/z_B})$$

There are two established methods for determination of the selectivity coefficient based on the separate and mixed solution methods.

2.8.6.1 Separate Solutions Method

In this method, the potential for the electrode is measured in solutions containing only ion A and then in solutions containing ion B. This method is very simple to perform but has the obvious disadvantage that it does not recreate the actual conditions in which an electrode would be used.

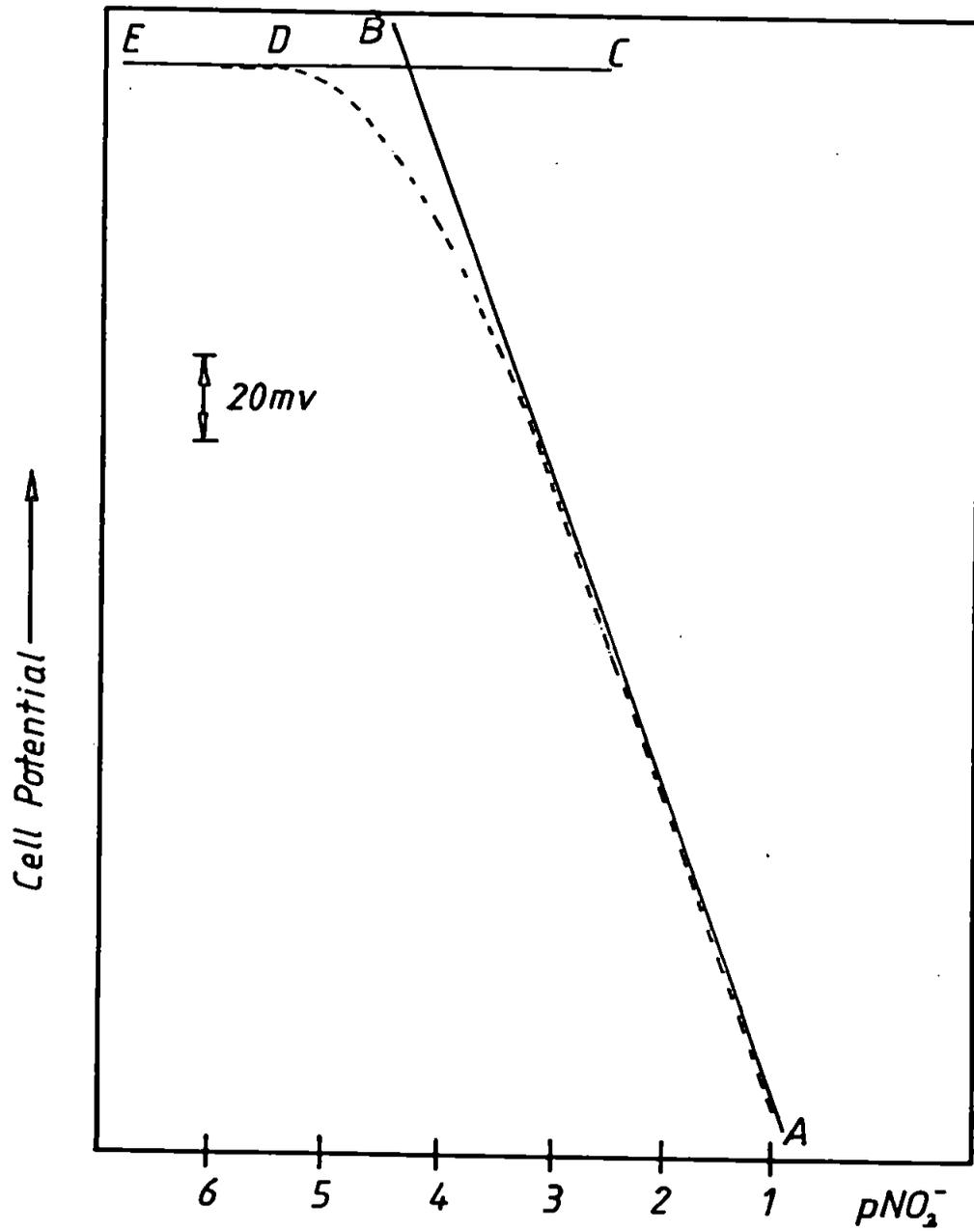
2.8.6.2 Mixed Solutions Method

The mixed solutions method overcomes the disadvantage with the separate solutions method and was utilised for all selectivity coefficient determinations in this work. Solutions were prepared with a fixed level of interferent and varying levels of the analyte. A calibration curve was prepared and the so called 18mV method was used [22]. From Fig. 2.6 the point at which AB varies from AD by 18mV is taken as the activity for A, a_A , and then substituted into the equation:

$$K_{A,B}^{\text{pot}} = \frac{a_A^{z_A}}{a_B^{z_B}}$$

Figure 2.6

Determination of Selectivity Coefficients



The value of 18mV for a monovalent ion is not an arbitrary figure but is calculated as follows:

When $K_{A,B}^{\text{pot}} = \frac{a_A^{z_A}}{a_B^{z_B}}$ both ions A and B are contributing equally to the response.

The electrode potential at this point is:

$$E = E^\circ + \frac{2.303RT}{z_A F} \log_{10} (a_A + K_{A,B}^{\text{pot}} a_B^{z_A/z_B})$$

$$= E^\circ + \frac{2.303RT}{z_A F} \log_{10} (2a_A)$$

The difference in electrode potentials in solutions of A at a_A both with and without B at a_B is therefore given by:

$$\Delta E = \frac{2.303RT}{z_A F} (\log_{10} 2a_A - \log_{10} a_A)$$

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

$$= \frac{18}{z_A} \text{ mV at } 298\text{K}$$

which for a monovalent anion is -18mV at 298K.

The alternative approach is to use the intersect method shown in fig. 2.6 with the point AB-CE to give a_A for replacement in the equation:

$$K_{A,B}^{\text{pot}} = \frac{a_A^{z_A}}{a_B^{z_B}}$$

for selected membranes, the $k_{\text{NO}_3^-, X^-}^{\text{pot}}$ or $k_{\text{NO}_3^-, X^{2-}}^{\text{pot}}$ value was determined for a range of common anions (X^- and X^{2-}) using either the potassium or sodium salt.

2.8.7 Limit of Detection

We have used the IUPAC recommended definition of limit of detection which is calculated from the calibration curve as shown in Fig. 2.6. Extrapolation of AB and CD gives rise to a point at the intersect to yield an activity for the primary ion. It is interesting to note that this is also used in the intersection method for the determination of $K_{A,B}^{\text{pot}}$. Limits of detection are influenced in many cases by interferences which cannot be removed from the sample. The slight solubility of the electroactive material will also restrict the detection limit and it is for this reason that covalent attachment was expected to yield improved values. The purity of the water and reagents used to prepare standards and samples will also affect detection limits.

2.9 Cross-link Density

The covalent attachment of the QAS was achieved at the same time as the introduction of inter-molecular cross-links between the polymer chains. These cross-links render the polymer insoluble in all solvents and the extent of swelling will depend on the extent of polymer-solvent interaction. Because polymers such as PVC do not contain inter-molecular cross-links, the action of a suitable solvent will result in polymer dissolution. As the solvent is absorbed into the polymer, the network is expanded. In the classical work of Flory and Rehner [109,110] the extent of solvent absorption can be related to the cross-link density using the following equation [109-111]:

$$V_2 = \frac{1}{1 + \left[\frac{\rho_2}{\rho_1} \right] S}$$

where:

V_2 = volume fraction of swollen polymer;

ρ_1 = solvent density;

ρ_2 = rubber density;

and

$$S = \frac{M - M_0}{M_0}$$

where:

M = membrane swollen weight;

M₀ = membrane weight after the swelling solvent was removed.

$$V_e = - [2.303 \log_{10} (1 - V_2) + V_2 + \chi V_2^2] [V_1 (V_2^{1/3} - V_2 / 2)]^{-1}$$

where:

V_e = cross-link density mol cross-link cm⁻³;

χ = the solvent-polymer interaction constant;

V₁ = molar volume of the solvent.

This is the so called unmodified Flory Rehner equation [109], based on the assumption that the number of intra-molecular cross-links is negligible. As the level of diluent, such as filler or plasticiser is increased the distance between polymer chains becomes larger. This increases the probability that intra-molecular cross-links are formed.

The value for V₂ was determined experimentally by measuring the density of membranes (ρ₂) based on both SBS and NBr polymers. The membranes were then immersed in an appropriate solvent at room temperature for 24 hours. For SBS the swelling solvent n-heptane (AnalaR BDH), was chosen whilst for the NBr membranes, ethylmethyl ketone (AnalaR BDH) was selected. These determinations were made in triplicate and the swollen weight was measured using a 4 decimal place balance (Mettler H-30)(Mettler, Zurich, Switzerland), placed on a purpose built marble weighing table. The balance weighing chamber was saturated with the appropriate solvent by placing

a small volume on a watch glass within the chamber. Each membrane was removed from the solvent gently dabbed with a tissue and immediately placed on the weighing pan to give value M . It was found that this operation needed to be carried out rapidly to avoid loss of solvent from the swollen membrane. After weighing, the membrane was placed on a watch glass and held at reduced pressure for 48 hours to give value M_0 . Membranes were weighed to constant mass after 48 and 72 hours immersion in the solvent to confirm that equilibrium swell had been achieved after 24 hours.

A solvent polymer interaction factor χ for SBS of 0.589 and a molar volume for n-heptane of 147.5cm^3 was used [85]. For the NBr rubber, because of the varying ACN levels, different values were used for each of the polymers. These had been previously determined from swelling data and enthalpy contributions calculated from solubility parameters [112]. Values existed for polymers with between 18 and 39% ACN levels and the values were calculated for the 50% ACN polymer by extrapolation of the data. The molar volume for ethylmethyl ketone was 89.6cm^3 and a solvent density of 0.805g cm^3 was used.

2.10 Conditioning Process - Determination of Bromide

During the conditioning of the membrane, bromide anions in the QAS were replaced by nitrate anions and as a result the membrane became permselective toward nitrate anions. To follow this process, approximately 0.15g of master membrane was conditioned in 2.5ml of 0.1M potassium nitrate solution. The determinations were made in duplicate and a sample of $100\mu\text{l}$ was taken over the conditioning period lasting up to 32 days. The test sample required dilution by a factor of 100 to give a solution

which could then be analysed by ion chromatography. An ion chromatograph (Data Unit 745B and HPLC Pump 501, Waters Chromatography, Milford, Massachusetts, USA), and conductivity detector (Model 430, Waters Chromatography) were used. Separation took place on an anion column (IC Pak A 5cm x 4.6mm 10 μ m), (Waters Chromatography). The injection loop was 100 μ l and a borate gluconate mobile phase was used. A borate gluconate concentrate was prepared by dissolving sodium gluconate (16g), boric acid (18g) and sodium tetraborate decahydrate (25g) in glycerol (250ml) and diluted with Nanopure water to 1 litre. The borate gluconate concentrate (20ml), n-butanol (20ml) and acetonitrile (120ml) were diluted with Nanopure water to 1 litre to give the borate gluconate eluent. Standards were prepared by serial dilution in distilled water (AnalaR, BDH) and contained between 1 and 16 ppm potassium bromide (AnalaR, BDH).

CHAPTER 3

Solvent Cast Membranes

3.1 Poly (Styrene-b-butadiene-styrene)

3.1.1 Composition

The poly(styrene-b-butadiene-styrene) (SBS) polymer had previously proved to be a very successful membrane matrix when used for both calcium and nitrate selective electrodes [80-85]. Two ion exchangers triallylethylammonium bromide (TAEAB) and triallylbutylammonium bromide (TABAB) had given the best results for the nitrate ISEs [85]. The electrodes exhibited a fast response, extended lifetime and were robust but a relatively poor selectivity for nitrate in the presence of interferents was a recognised limitation.

These two ion exchangers were selected for further evaluation in the present study. Membranes were fabricated using the established solvent casting technique. A period of heating in a hot air oven was included to initiate the cross-linking reaction. The composition and appearance of the SBS membranes are shown in Table 3.1 which, did not include a solvent mediator.

Table 3.1

Composition and Appearance of Solvent Cast SBS Membranes

Membrane Number	TAEAB/ pphr* (%mm/m)	TABAB/ pphr (%mm/m)	TBHP/ pphr (%m/m)	Membrane Appearance
SBS A	-	-	-	Rigid membrane
SBS B	-	-	1.1 (1.2)	Rigid membrane
SBS C	10.2 (9.1)	-	1.1 (1.2)	Rigid membrane
SBS D	10.2 (8.8)	-	6.2 (5.3)	Rigid membrane
SBS E	10.2 (8.2)	-	14.7 (11.8)	Rigid membrane
SBS F	-	11.9 (10.0)	1.1 (1.0)	Rigid membrane
SBS G	-	11.9 (10.0)	6.2 (5.3)	Rigid membrane
SBS H	-	11.9 (9.4)	14.7 (11.6)	Rigid membrane

* pphr - parts per hundred of rubber

The introduction of either TAEAB or TABAB appeared to make the membrane surface slightly tacky. This may have been caused by surface exudate of either uncross-linked QAS, cross-linking agent or a reaction product. The use of TBHP in membrane SBS B produced a more resilient and elastic membrane than was provided by the thermoplastic elastomer on its own.

3.1.2 Electrode Response

Individual 7mm discs were punched from the master membranes SBS A to SBS H and conditioned for 24 hours as follows:

- 1 potassium nitrate solution ($10^{-1}M$) (BDH) - nitrate responsive;
- 2 potassium chloride solution ($10^{-1}M$) (BDH) - chloride responsive;
- 3 potassium bromide solution ($10^{-1}M$) (BDH) - bromide responsive;
- 4 sodium perchlorate solution ($10^{-1}M$) (BDH) - perchlorate responsive.

The electrode response of the conditioned membranes was determined in pure solutions using the sodium or potassium salt of the anion of interest. Results are shown in Table

3.2.

Table 3.2**SBS Membrane Electrode Response**

Membrane Number	Nitrate ISE slope/mV decade ⁻¹	Chloride ISE slope/mV decade ⁻¹	Bromide ISE slope/mV decade ⁻¹	Perchlorate ISE slope/mV decade ⁻¹
SBS A	Unresponsive	Unresponsive	Unresponsive	Unresponsive
SBS B	Unresponsive	Unresponsive	Unresponsive	Unresponsive
SBS C	-15.6	-50.7	Unresponsive	Unresponsive
SBS D	Unresponsive	-49.7	-42.4	Unresponsive
SBS E	-57.1	-49.0	-43.9	-21.5
SBS F	-38.3	-42.4	-38.3	Unresponsive
SBS G	-42.5	-48.5	-37.3	-14.6
SBS H	-51.0	-39.6	Punctured	-24.7

SBS membranes A and B confirmed that the polymer and or cross-linking agent were not electroactive even after conditioning for the anions of interest. When the QAS was introduced some of the membranes became permselective. Of the electrodes tested, only membrane SBS E produced a Nernstian response to nitrate anions when conditioned appropriately. The added ion exchanger was TAEAB which after conditioning was expected to have been predominantly in the nitrate form.

The response of the different membrane compositions appeared to be erratic and did not follow any simple overall pattern. Membranes F to H would suggest that an

increase in cross-linking agent and therefore a theoretical rise in cross-link density had a beneficial effect for the nitrate responsive electrode. However, results for membranes C to E based on TAEAB do not support this theory.

With appropriate conditioning the SBS membranes have become permselective to nitrate, chloride, bromide and perchlorate anions. This is one of the recognised disadvantages of an ion exchanger based electrode. The relative ease with which a membrane can be made responsive to a range of anions, inevitably affects the potential for a highly selective response.

The selectivity coefficient $k_{NO_3^-, Cl^-}^{pot}$ was calculated for certain SBS membranes using the mixed solution method and the 18mV method [22]. A constant interferent of $10^{-1}M$ potassium chloride was added to the nitrate standards. The results are shown in Table 3.3.

Table 3.3

Selectivity Data for SBS Membrane Electrodes

Membrane Number	$k_{NO_3^-, Cl^-}^{pot} *$	Composition Notes Added ion exchanger
SBS E	2.1×10^{-1}	TAEAB
SBS G	1.6×10^{-1}	TABAB
SBS H	1.6×10^{-1}	TABAB

*A constant interferent of $10^{-1}M$ potassium chloride was used.

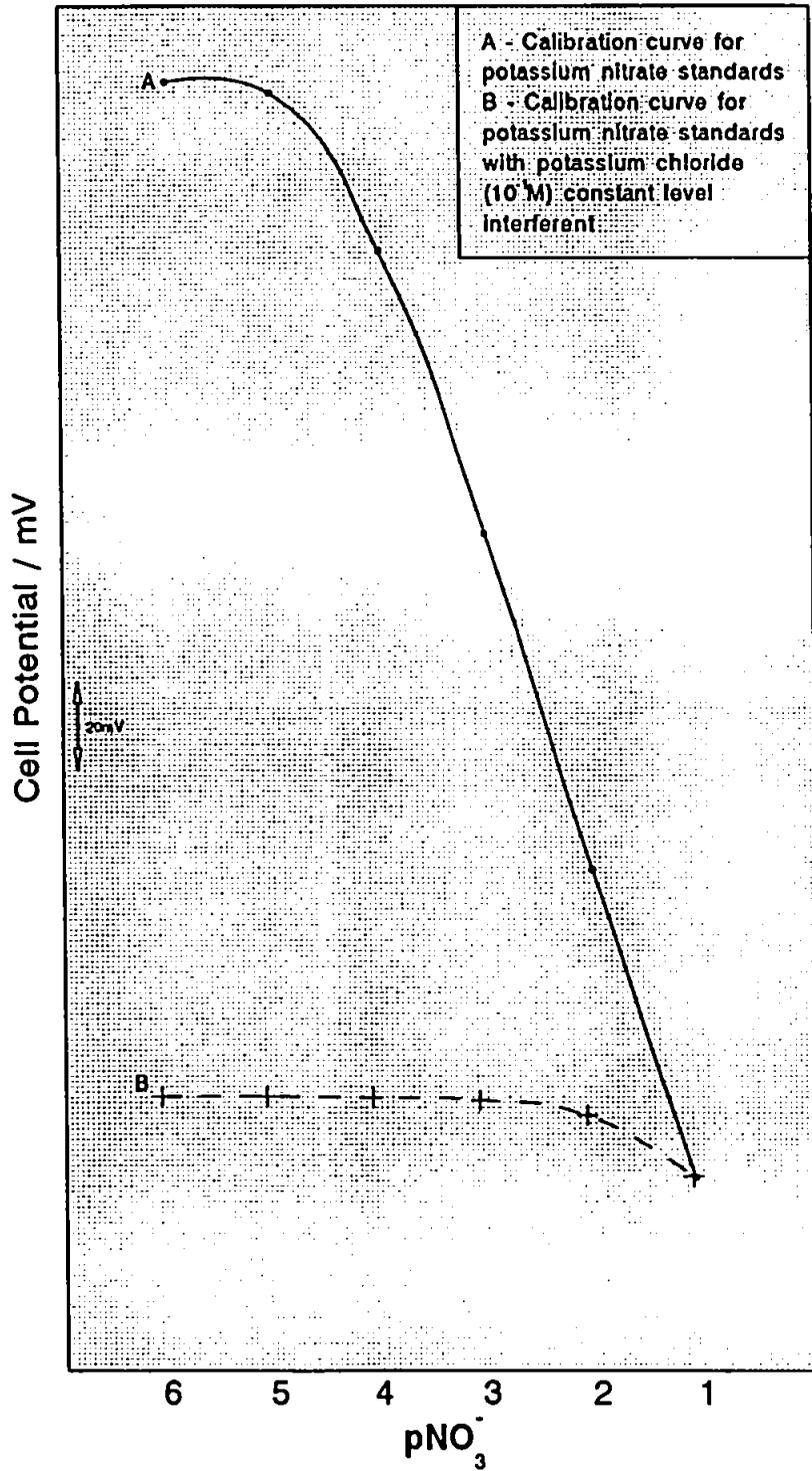
The selectivity coefficients were similar to those recorded by King [85] who found the best $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ of 1.6×10^{-1} using potassium chloride (10^{-3}M) as the interferent and the mixed solutions method. The selectivity coefficient was regarded as the limiting factor for the application of these SBS membranes. A calibration curve for the best Nernstian responsive nitrate electrode with membrane SBS E is shown in fig. 3.1 together with the response in the presence of potassium chloride (10^{-1}M) as an interferent.

3.1.3 Cross-link Density

To characterise further the individual membranes the cross-link density values were determined based upon the Flory-Rehner equation [109-111]. The individual membranes were swollen in n-heptane to enable the so called swollen weight to be measured. For a material with a three dimensional network a solvent can only swell the matrix. Dissolution of the polymer is impossible because of the cross-linked network. For the SBS membranes, partial dissolution of the membrane occurred which prevented the determination of the swollen membrane weight. The effect was more pronounced on the membrane surface. This may have had the lowest level of cross-links due to the quenching effect from atmospheric oxygen. From this data it is possible to conclude that the SBS membranes evaluated contained a relatively low level of cross-links. The immobilisation process relied on the electroactive QAS becoming covalently bound during the cross-linking reaction. It is therefore possible that a low level of electroactive material was actually covalently bound with the remainder simply being entrapped within the SBS polymer. The SBS membranes displayed a very marked two sided response with slopes varying by up to -30mV decade^{-1} .

Figure 3.1

Calibration Curve for a Nitrate Selective Electrode with SBS Membrane E



3.2 Poly (Acrylonitrile-butadiene)

3.2.1 Composition

The use of SBS as the polymer matrix produced nitrate sensitive ISEs but with poor selectivity. Moody *et al* [50] believed this was due to the omission of a solvent mediator from the membrane composition. The solvent mediators typically used for nitrate ISEs were incompatible with the SBS. An alternative polymer matrix poly(acrylonitrile-butadiene) (NBr) was selected which was predicted to be compatible with the polar solvent mediators. The unsaturation in the butadiene would enable the novel free radical based immobilisation technique to be used to cross-link the polymer. When cross-linked, NBr was expected to produce robust membranes suitable for assembly into an electrode tip.

A range of membranes were fabricated using (NBr) as the matrix. The same modified solvent casting technique was used together with a period of heating in an air oven. TAEAB and TABAB were selected as the electroactive materials. The cross-linking agent was TBHP and the membranes were fabricated without a solvent mediator. The composition and appearance of the membranes are shown in Table 3:4.

The use of the cross-linking agent TBHP resulted in an elastic and resilient membrane. Poor mechanical strength of the membrane resulted when any of the five solvent mediators from section 2.6.2 were introduced into the composition. Very elastic and sticky membranes were produced using only 33pphr (20% m/m) solvent mediator. Assembly in the electrode housing resulted in distortion or ballooning of the membrane under pressure.

Table 3.4

Effect of Membrane Composition on Physical Properties and Cross-link Density

Membrane Number	TAEAB/pphr (% m/m)	TABAB/pphr (% m/m)	TBPH/pphr (% m/m)	Appearance	Cross-link Density/mol cross-links cm ⁻³
C1	-	-	-	stretchy transparent cream	soluble
C2	10.2 (9.1)	-	1.1 (1.2)	elastic transparent yellow	1.1 x 10 ⁻⁵
C3	10.2 (8.8)	-	6.2 (5.3)	elastic transparent yellow	1.6 x 10 ⁻⁵
C4	10.2 (8.2)	-	14.7 (11.8)	elastic transparent yellow	2.3 x 10 ⁻⁵
C5	-	11.9 (10.5)	1.1 (1.0)	elastic transparent yellow	0.8 x 10 ⁻⁵
C6	-	11.9 (10.0)	6.2 (5.3)	elastic transparent yellow	1.3 x 10 ⁻⁵
C7	-	11.9 (9.4)	14.7 (11.6)	elastic transparent yellow	1.8 x 10 ⁻⁵
C8	-	11.9 (10.6)	-	stretchy transparent membrane	-
C9	10.2 (9.2)	-	-	stretchy transparent membrane	-

The use of a solvent mediator had two definite effects on mechanical strength. Firstly, there is the softening of the rubber by the addition of a relatively low molecular weight liquid. Secondly, the solvent mediator acts as a diluent within the rubber matrix. Individual polymer chains are forced further apart and there is a greater probability that intra-molecular cross-links are formed rather than inter-molecular bonds. These intra-chain polymer links do not contribute to the effective mechanical properties of the rubber. It is expected that the softening effect of the solvent mediator is the major contributor to the poor mechanical properties experienced with the membranes.

3.2.2 Electrode Response

Individual 7mm discs were punched out from the master membrane and required conditioning for 1 week in 10^{-1} M potassium nitrate solution to produce functioning electrodes. SBS membranes had previously only required 1 day to condition and effect the replacement of nitrate anions for bromide. The electrode responses of the membranes to potassium nitrate standards are summarised in Table 3.5. Due to the relatively poor selectivity shown in section 3.1.2 the level of potassium chloride interferent was reduced from 10^{-1} to 10^{-2} M.

Table 3.5**Nitrate Electrode Response of Solvent Cast NBr Membranes**

Membrane Number	Slope/mV Decade ⁻¹	*Limit of Detection/M	$k_{NO_3^-, Cl^-}^{pot}$	Added ion exchanger
C1	unresponsive	-	-	none
C2	-54.2	6.0×10^{-5}	-	TAEAB
C3	-57.3	1.2×10^{-4}	1.9×10^{-2}	TAEAB
C4	-51.3	7.0×10^{-4}	-	TAEAB
C5	-57.0	1.7×10^{-4}	1.8×10^{-2}	TABAB
C6	-57.7	2.4×10^{-5}	1.6×10^{-2}	TABAB
C7	-59.2	2.5×10^{-5}	1.3×10^{-2}	TABAB
C8	-51.6	2.0×10^{-5}	1.3×10^{-2}	TABAB
C9	-37.5	-	-	TAEAB

* Limit of detection as defined in reference [22].

Constant interferent level of 10^{-2} M KCl.

The membrane C1 composed of only polymer was non-functioning even after appropriate conditioning. The use of TAEAB produced two electrodes C2 and C4 with sub-Nernstian responses. TABAB appeared to be a superior electroactive component because all 3 fabricated membranes C5, C6 and C7 containing the cross-linking agent TBHP, produced electrodes with a Nernstian response. The use of

NBr as the polymer matrix produced superior electrodes to those fabricated using SBS. There was a significant improvement in the selectivity coefficient $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ from 1.6×10^{-1} to 1.3×10^{-2} . The value for the NBr electrode compares very favourably to that of a commercially available nitrate selective PVC electrode (Philips Analytical). A $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ value of 1.2×10^{-2} was obtained for this commercial electrode under the same experimental conditions. A calibration curve for the best Nernstian responsive nitrate electrode with NBr membrane C7 is shown in fig. 3.2 together with the response in the presence of potassium chloride (10^{-2}M) as an interferent.

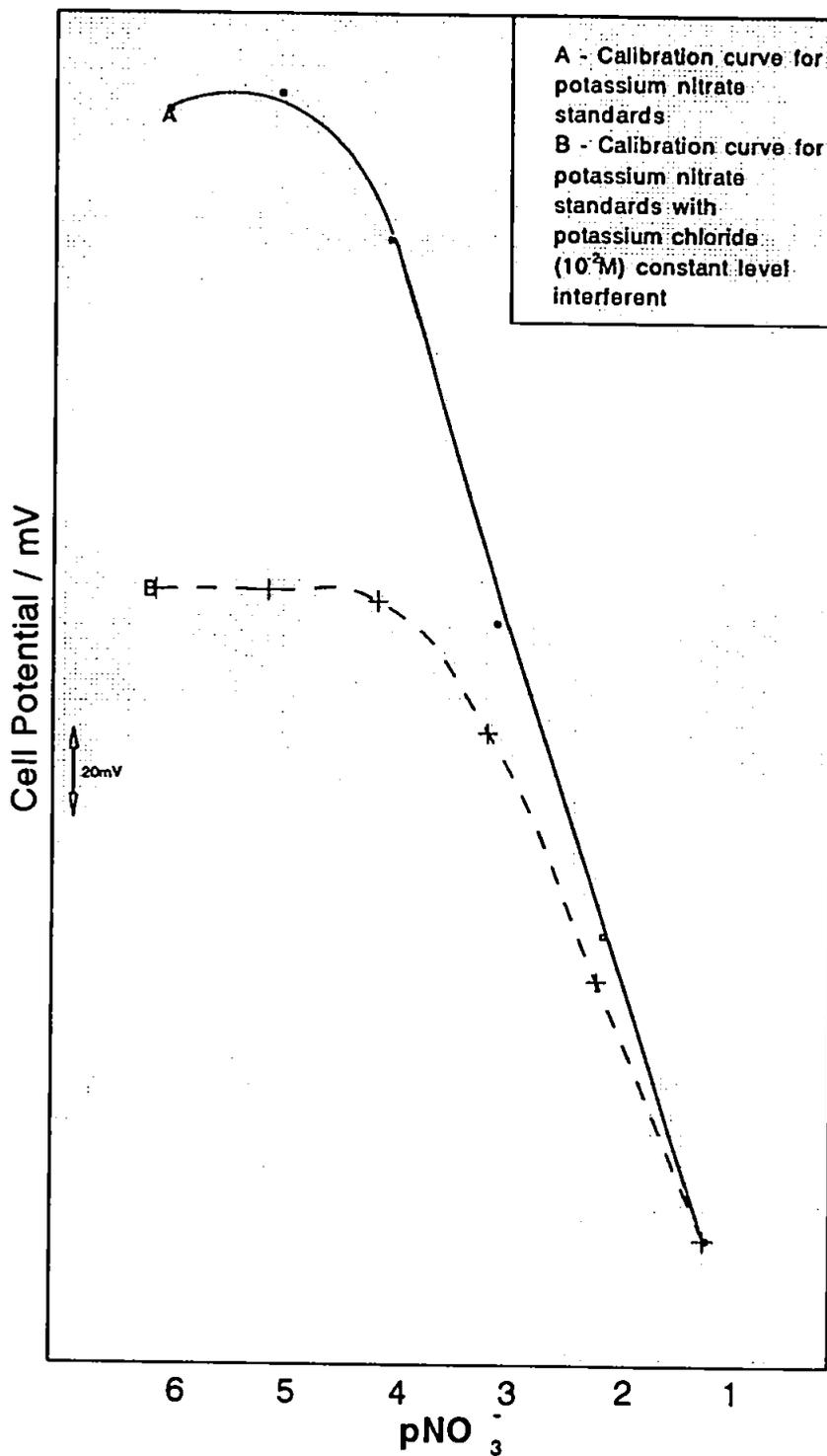
The addition of higher levels of TBHP for the TABAB membranes C5 - C7 resulted in a slight improvement in selectivity. At the same time the limit of detection also improved. The limit of detection for a PVC membrane electrode is influenced by both solubility of the ion exchanger and the presence of interferents. The improvement in detection limit may have occurred because of the increased cross-link formation. This would have covalently bound more QAS groups to the polymer network. Alternatively the cross-links may have effectively locked in any entangled ion exchanger and reduced the rate of diffusion and dissolution from the membrane.

The use of 2-NPOE (bpt 197°C) at 20% m/m produced a membrane with poor physical strength such that it ruptured during evaluation. A solvent cast membrane containing the same level of DBP (bpt 340°C) was however sufficiently robust to enable the electrode response to be determined before failure. After appropriate conditioning a slope of $-57.9 \text{ mV decade}^{-1}$ was obtained and a selectivity coefficient $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ of 3.5×10^{-2} was recorded. The addition of a solvent mediator had not in this case

Figure 3.2

Calibration Curve for a Nitrate Selective Electrode with Solvent Cast

NBr Membrane C7



resulted in an improvement in selectivity. Decan-1-ol (bpt 229°) presented problems of incompatibility with the polymer. This was characterised by the formation of a greasy film on the membrane surface. A problem of solvent mediator volatility was noted with chlorobenzene (bpt 132°). This was confirmed by infrared studies using both attenuated total reflectance and transmission through the stretched membrane. The membrane gave nitrate responsive electrodes with a slope of - 47.1 mV decade⁻¹ when tested in potassium nitrate standards. The addition of the solvent mediator to the membrane composition reduced the viscosity of the casting solution. On pouring it was noted that there was a high level of seepage under the glass ring. This resulted in a thin membrane which exacerbated the poor physical properties. When the membranes were conditioned for 7 days in 10⁻¹M potassium chloride, the electrodes were responsive to chloride anions. Test results are shown in Table 3.6.

Table 3.6

Chloride Electrode Response of Solvent Cast NBr Membranes

Membrane Number	Slope/Mv decade ⁻¹	Composition Notes/(pphr)
C1	Unresponsive	NBr
C2	-9.5	TAEAB TBHP (1.1)
C3	-47.0	TAEAB TBHP (6.2)
C4	-27.9	TAEAB TBHP (14.7)
C5	-18.3	TABAB TBHP (1.1)
C6	-26.3	TABAB TBHP (6.2)
C7	-15.6	TABAB TBHP (14.7)

The response to chloride anions was overall very poor whilst membrane C3 based on TAEAB gave the best result. Both the chloride and nitrate sensitive electrodes gave a pronounced two-sided response. After conditioning one side of the membrane was noticeably lighter than the other. It appeared that the lighter membrane side always gave a lower response when mounted in the electrode such that it was exposed to the test solution. The effect of the two-sided response for a given membrane could be as high as -20 or -30 mV decade⁻¹. This pronounced two-sided response was believed to be a function of the fabrication technique because a similar phenomenon was observed with solvent cast SBS membranes. Initiating the cross-linking reaction in an air oven presents a very different environment to the two sides of the membrane. It was considered desirable to modify the fabrication technique to overcome the pronounced two sided behaviour.

3.2.3 Cross-link Density

The cross-link density for membranes C1 - C7 was determined using ethylmethyl ketone (EMK) as the swelling solvent. Results are shown in Table 3.7

The individual membranes after swelling in EMK were evaluated for electrode response using potassium nitrate standards. This was considered to represent a quick means of establishing the extent of immobilised ion exchanger. In theory unbound QAS would be leached from the membrane and the response impaired. Membranes C2 and C5 could not be evaluated because they tore during the solvent swelling process. This involved the individual membranes absorbing more than 400% by mass of EMK. In

the highly swollen state the membranes were very fragile and susceptible to tearing. The results were inconclusive but indicated that a higher level of TBHP enhanced the membrane response after extraction with EMK. This may have occurred because more QAS was covalently bound because of the increased level of free radicals produced. These results do not preclude the possibility that other materials were extracted from the membrane impairing the electrode response

Table 3.7

Cross-link Density Values for Solvent Cast NBr Membranes

Membrane Number	Cross-link density/mol cross-link cm ⁻³	EMK extracted slope/mV decade ⁻¹	Composition Notes
C1	Soluble	---	---
C2	1.1 x 10 ⁻⁵	Torn	TAEAB
C3	1.6 x 10 ⁻⁵	-34.2 (-57.3)*	TAEAB
C4	2.3 x 10 ⁻⁵	---	TAEAB
C5	0.8 x 10 ⁻⁵	Torn	TABAB
C6	1.3 x 10 ⁻⁵	Unresponsive (-57.7)	TABAB
C7	1.8 x 10 ⁻⁵	-21.9 (-59.2)	TABAB

*Original results in parenthesis

The cross-link density values indicated that increasing levels of the hydroperoxide, TBHP, produced an increase in the number of cross-links. The actual value for

cross-link density could be considered somewhat low in relation to the level of initiator used. Comparison with literature values suggest that a cross-link density in the region of 8×10^{-5} mol cross-links cm^{-3} may have been more normal [111]. This may be due to the use of TBHP as the initiator or the relatively low temperature for activation. The $t_{1/2}$ lifetimes for TBHP in Table 3.8 suggest that temperatures in excess of 100°C are necessary to generate a significant number of free radicals.

Table 3.8

Half life data for Free Radical Formation

Temperature $^{\circ}\text{C}$	TBHP $t_{1/2}$ / hours	DCP $t_{1/2}$ / hours
90	-	-
100	165	100
110	42	25
120	12	6.7
130	3.2	1.8
140	1.0	0.5
150	0.3	0.1

Alternatively it is possible that there are competitive reactions which may not possibly result in cross-link formation. One such reaction could be a quenching reaction between a polymer chain radical and QAS radical. This would result in covalently bound QAS but not produce an inter-molecular cross-link. It was expected that an increase in cross-link density would improve mechanical strength and allow an increased incorporation of solvent mediator. For these reasons together with the pronounced two sided response, an alternative fabrication technique and organic

peroxide was considered necessary. Dicumyl peroxide is a more conventional free radical initiator and from the data in Table 3.8, generates free radicals more readily at a given temperature than TBHP.

CHAPTER 4

Hot Pressed Membranes

4.1 Development

4.1.1 Composition

The pronounced two-sided response characteristic of solvent cast membranes was a severe limitation, and the technique of hot pressing membranes was therefore developed with the aim of eliminating this undesirable feature. A higher level of cross-linking was also expected to result which would produce a harder, more robust membrane. This in turn should enable the use of a higher level of solvent mediator to be incorporated in the membrane.

Membranes were fabricated using the method described in 2.7.2 and contained the 50% ACN polymer poly(acrylonitrile-butadiene) (NBr), triallylbutylammonium bromide (TABAB), tert.-butylhydroperoxide (TBHP) with varying levels of solvent mediator. The use of 65% m/m and 57% m/m of solvent mediator produced membranes with surface tack. This was due to the pronounced softening effect caused by the incorporation of a high level of solvent mediator. The use of 40% m/m solvent mediator gave tack free membranes with excellent mechanical strength. It was established that all traces of solvent needed to be removed prior to hot pressing. This avoided the formation of small air-bubbles within the membrane. The hot pressed membranes had a very characteristic odour which was believed to be bromine. When a hot pressed membrane was fabricated without the QAS present there was no characteristic odour. The composition of the fabricated membranes are shown in Table 4.1.

Table 4.1**Composition of Hot Pressed Membranes with 50% ACN NBr Polymer**

Membrane Number	TABAB/%m/m (pphr)	TBHP/%m/m (pphr)	Solvent Mediator/%m/m (pphr)
H1	9.3 (11.9)	11.6 (14.7)	none
H2	5.7 (11.9)	7.0 (14.7)	nitrobenzene 39.7 (83.4)
H3	5.7 (11.9)	7.0 (14.7)	chlorobenzene 39.7 (83.4)
H4	5.7 (11.9)	7.0 (14.7)	DBP 39.7 (83.4)
H5	5.7 (11.9)	7.0 (14.7)	decan-1-ol 39.7 (83.4)
H6	5.7 (11.9)	7.0 (14.7)	2-NPOE 39.7 (83.4)
H7	nil	7.4 (14.7)	DBP 42.1 (83.4)

Membranes H2 and H6 were not sufficiently robust to allow subsequent evaluation. The decan-1-ol membrane H5 produced a greasy film on the surface. This was caused by poor compatibility between the NBr polymer and decan-1-ol.

4.1.2 Electrode Response

After appropriate conditioning the response to potassium nitrate solutions was evaluated. Results are shown in Table 4.2.

Table 4.2**Nitrate Electrode Response of Hot Pressed NBr Membranes**

Membrane Number	Slope/mV decade ⁻¹	Limit of Detection/M	$k_{NO_3^-, Cl^-}^{pot}$	Solvent Mediator
H1	-54.6	3.1×10^{-5}	1.1×10^{-2}	none
H2	Tom	-	-	nitrobenzene
H3	-43.1	5.6×10^{-5}	1.1×10^{-2}	chlorobenzene
H4	-51.9	4.0×10^{-5}	1.2×10^{-2}	DPB
H5	-42.5	5.6×10^{-5}	1.5×10^{-2}	decan-1-ol
H6	Tom	-	-	2-NPOE
H7	-10.8	-	-	DPB

The response to nitrate was sub-Nernstian for all membranes tested. Interestingly the solvent mediator appeared capable of giving a very small potential without an ion exchanger present as shown in membrane H7. Membranes conditioned in $10^{-1}M$ potassium chloride for 7 days produced electrodes which were unresponsive to potassium chloride solutions.

4.1.3 Cross-link Density

The cross-link density for membranes H1 and H4 was determined using EMK as the swelling solvent. Values of 1.3×10^{-5} and 0.12×10^{-5} mole cross-links per cm^3 were found respectively. These figures suggested a relatively low cross-link density and prompted the evaluation of an alternative initiator.

Tert.-butylhydroperoxide (TBHP) (available as a 70% aqueous solution) was replaced in the membrane composition by dicumyl peroxide (DCP). The replacement was on the basis of an equivalent number of free radicals being produced by dicumyl peroxide. Each DCP molecule formed two free radicals as opposed to effectively only one free radical for each TBHP molecule, as shown in Fig. 4.1 below:

Figure 4.1

Free Radical Formation

From Hydroperoxide where R = tert-butyl group



From Peroxide where R = cumyl group



Comparison of half life ($t_{1/2}$) data in Table 3.8 in section 3.2.3 showed that DCP would generate more free radicals at the hot pressing temperature of 150°C. This should therefore result in increased cross-link formation and would be expected to covalently bond more QAS to the polymer chain.

4.2 High ACN Content Hot Pressed NBr Membranes

Hot pressed membranes were successfully fabricated using high ACN NBr as the polymer matrix. In Section 4.1.1 membranes were described using TBHP as the free radical initiator. This was replaced stoichiometrically by dicumyl peroxide based on the highest level of TBHP used in the solvent cast membranes C4 and C7.

4.2.1 Composition

The composition of the hot pressed membranes was investigated using TABAB as the added ion exchanger. The most promising solvent mediators were then evaluated with TAEAB. Membranes with an increased level of decan-1-*ol* were not fabricated because of compatibility problems. This incompatibility was characterised by the formation of a greasy film on the membrane surface. The composition of the fabricated membranes are shown in Table 4.3

Table 4.3

Composition of NBr Membranes Incorporating a Solvent Mediator

Membrane Number	TABAB/% m/m (pphr)	DCP/%m/m (pphr)	Solvent Mediator/%m/m (pphr)
H8	5.6 (11.9)	7.3 (15.5)	nitrobenzene 39.5 (83.4)
H9	5.6 (11.9)	7.3 (15.5)	chlorobenzene 39.5 (83.4)
H10	5.6 (11.9)	7.3 (15.5)	DBP 39.5 (83.4)
H11	5.6 (11.9)	7.3 (15.5)	decan-1-ol 39.5 (83.4)
H12	5.6 (11.9)	7.3 (15.5)	2-NPOE 39.5 (83.4)
H13	3.3 (11.9)	4.3 (15.5)	nitrobenzene 64.7 (233.4)
H14	3.3 (11.9)	4.3 (15.5)	chlorobenzene 64.7 (233.4)
H15	3.3 (11.9)	4.3 (15.5)	DBP 64.7 (233.4)
H16	3.3 (11.9)	4.3 (15.5)	2-NPOE 64.7 (233.4)

The membranes fabricated with 64.7% m/m solvent mediator lacked physical strength. In particular those based on DBP and 2-NPOE tore during assembly into the electrode tip. The optimum solvent mediator level was set at 40% m/m and used for further membrane fabrication with TAEAB. With chlorobenzene there was a pronounced problem of volatility confirmed by examination of membrane H 9 by infrared spectrophotometry (IR). An IR spectrophotometer (IR 782 Perkin Elmer, Beaconsfield, England) was used to record the IR spectrum. Absence of absorption bands characteristic of chlorobenzene were interpreted as confirmation of volatilisation of the solvent mediator during the fabrication and hot pressing process. Decan-1-ol had

a poor compatibility with the NBr polymer. For these reasons only nitrobenzene, DBP and 2-NPOE were selected for the fabrication of further membranes and the compositions are shown in Table 4.4.

Table 4.4

Composition of High ACN Content NBr Membranes

Membrane Number	TAEAB/ %m/m (pphr)	TABAB/ %m/m (pphr)	DCP/ %m/m (pphr)	Solvent Mediator
H17	-	8.3 (11.9)	12.2 (15.5)	none
H18	8.1 (10.2)	-	12.3 (15.5)	none
H19	4.9 (10.2)	-	7.4 (15.5)	nitrobenzene 40.0 (83.8)
H20	4.9 (10.2)	-	7.4 (15.5)	DBP 40.0 (83.8)
H21	4.9 (10.2)	-	7.4 (15.5)	2-NPOE 40.0 (83.8)

4.2.2 Electrode Response

The electrode response of nitrate sensitive membranes was evaluated in potassium nitrate standards containing potassium dihydrogen phosphate (10^{-2}M) as an ionic strength adjustment buffer (ISAB). The selectivity co-efficient $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ was determined using the mixed solutions method and a constant interferent level of potassium chloride (10^{-2}M) was used. Results are summarised in Tables 4.5, 4.6 and 4.7.

Table 4.5

Nitrate Electrode Response of NBr Membranes with 40% m/m Solvent Mediator

Membrane Number	Slope/mV decade ⁻¹	Limit of detection/M	$k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$	Composition Notes
H8	-59.6	5.6×10^{-5}	1.3×10^{-2}	TABAB nitrobenzene
H9	-57.6	5.6×10^{-5}	1.3×10^{-2}	TABAB chlorobenzene
H10	-58.2	3.9×10^{-5}	1.0×10^{-2}	TABAB DBP
H11	-57.4	6.3×10^{-5}	1.7×10^{-2}	TABAB decan-1-ol
H12	-58.4	3.0×10^{-5}	1.2×10^{-2}	TABAB 2-NPOE
H19	-57.0	2.5×10^{-5}	1.1×10^{-1}	TAEAB nitrobenzene
H20	-59.0	5.6×10^{-5}	3.3×10^{-2}	TAEAB DBP
H21	-57.9	4.8×10^{-5}	2.0×10^{-2}	TAEAB 2-NPOE

Table 4.6

Nitrate Electrode Response of NBr Membranes with 65% m/m Solvent Mediator

Membrane Number	Slope/mV decade ⁻¹	Limit of Detection/M	$k_{NO_3^-, Cl^-}^{pot}$	Composition Notes
H13	-55.5	1.6×10^{-5}	1.3×10^{-2}	TABAB nitrobenzene
H14	-60.8	1.3×10^{-5}	1.3×10^{-2}	TABAB chlorobenzene
H15	tore	-	-	TABAB DBP
H16	tore	-	-	TABAB 2-NPOE

Table 4.7

Nitrate Electrode Response of Solvent Mediator Free NBr Membranes

Membrane Number	Slope/m decade ⁻¹	Limit of Detection/M	$k_{NO_3^-, Cl^-}^{pot}$	Composition Notes Ion Exchanger
H17	-58.9	5.6×10^{-6}	1.3×10^{-2}	TABAB
H18	-58.1	3.2×10^{-5}	2.7×10^{-2}	TAEAB

All of the hot pressed membranes fabricated using DCP as the cross-linking agent gave a Nernstian response to potassium nitrate standards. There was no evidence of the two sided response which was characteristic of the solvent cast membranes. A good selectivity for nitrate was noted in the presence of 10^{-2} M potassium chloride solution. The values compared favourably with that obtained for the commercially available Philips PVC nitrate ISE of $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}} = 1.2 \times 10^{-2}$. The comparison of membranes both with and without solvent mediator are possible from the data in Tables 4.5, 4.6 and 4.7. The introduction of a solvent mediator had little effect on the Nernstian response, limit of detection and perhaps surprisingly the $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ value. Of the mediators evaluated, decan-1-ol had a serious compatibility problem which resulted in a surface exudate forming on the membrane. Chlorobenzene was volatile and volatilised during the fabrication and hot pressing process.

4.2.3 Selectivity Coefficients

The membranes that gave the best Nernstian performance were evaluated for selectivity coefficients $k_{\text{NO}_3^-, \text{X}^-}^{\text{pot}}$ and $k_{\text{NO}_3^-, \text{X}^{2-}}^{\text{pot}}$ for a range of common anions (X^- and X^{2-}). The mixed solutions method was used. The sodium or potassium salt of the anion was added at a constant level indicated in Table 4.8.

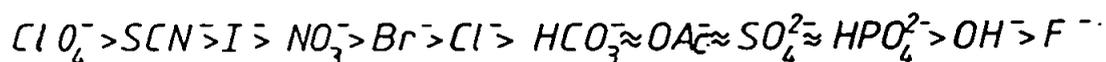
Table 4.8

Nitrate Electrode Selectivity Data for High ACN Content NBr Membranes

Anion X (Conc. _n /M)	$k_{NO_3^-, X^-}^{pot}$ or $k_{NO_3^-, X^{2-}}^{pot}$						Commercial Electrode*
	Membrane H8	Membrane H10	Membrane H12	Membrane H17	Membrane H18	Membrane H21	
F ⁻ (10 ⁻²)	4.4 x 10 ⁻²	4.4 x 10 ⁻³	1.9 x 10 ⁻³	5.2 x 10 ⁻⁴	2.2 x 10 ⁻²	1.5 x 10 ⁻²	10 ⁻⁴
Cl ⁻ (10 ⁻²)	1.3 x 10 ⁻²	10 ⁻²	1.2 x 10 ⁻²	1.3 x 10 ⁻²	2.7 x 10 ⁻²	2.0 x 10 ⁻²	10 ⁻²
Br ⁻ (10 ⁻²)	7.6 x 10 ⁻²	8.9 x 10 ⁻²	8.9 x 10 ⁻²	4.0 x 10 ⁻²	1.6 x 10 ⁻²	7.9 x 10 ⁻²	0.3
I ⁻ (10 ⁻⁴)	6.2	2.0	2.5	1.4	1.5	2.0	10
SCN ⁻ (10 ⁻⁴)	1.6	3.5	15	4.3	0.9	20	40
C104 ⁻ (10 ⁻⁴)	3.2	2.0	1.2	3.3	1.2	0.25	600
MnO ₄ ⁻ (10 ⁻⁶)	130	50	60	470	320	49	63
HCO ₃ ⁻ (10 ⁻¹)	3.9 x 10 ⁻³	6.3 x 10 ⁻³	1.1 x 10 ⁻²	5.2 x 10 ⁻⁵	1.8 x 10 ⁻³	10 ⁻²	4 x 10 ⁻⁴
NO ₂ ⁻ (10 ⁻²)	-	7.9 x 10 ⁻²	7.9 x 10 ⁻²	5.9 x 10 ⁻²	2.8 x 10 ⁻²	5.9 x 10 ⁻²	5 x 10 ⁻²
SO ₄ ²⁻ (10 ⁻¹)	4.4 x 10 ⁻³	4.0 x 10 ⁻⁴	7.1 x 10 ⁻⁴	2.5 x 10 ⁻³	3.2 x 10 ⁻⁴	3.9 x 10 ⁻⁴	10 ⁻⁴
Composition Notes	TABAB Nitrobenzene	TABAB DBP	TABAB 2-NPOE	TABAB None	TAEAB None	TAEAB 2-NPOE	

*Commercially available PVC membrane Nitrate Selective Electrode (Philips).

Overall the membranes showed selectivity broadly in accordance with the Hofmeister lipophilic series for anions [33]. The Hofmeister lipophilic series for anions is as follows:



Lipophilicity is defined as the partition coefficient between octan-1-ol and water. For the nitrate ISE based on an ion exchanger, it was found that ClO_4^- , SCN^- and I^- all significantly interfered with the electrode response. The $k_{NO_3^-, X^-}^{pot}$ value for these anions was greater than one, whilst for those anions to the right hand side of nitrate the value was less than unity. The range of selectivity values from ClO_4^- to SO_4^{2-} can be as large as 10^5 . The introduction of highly polar solvent mediators are claimed to reduce this to only 10 [33]. In many applications it would be desirable to have anti-Hofmeister selectivity. Ion exchange electroactive materials all follow the Hofmeister series and neutral or charged carrier based membranes are necessary to provide anti-Hofmeister behaviour.

The NBr polymer matrix membranes compared favourably with the results for the commercially available Philips PVC nitrate ISE. The membranes show a much lower level of interference from both ClO_4^- , SCN^- and Br^- . At the other end of the lipophilic series, the fluoride anion presented a higher level of interference. This difference in

behaviour may be a function of the ion exchanger or the cross-linked membrane. The 3-dimensional network may be more difficult to enter for large bulky anions. The smaller fluoride anion may have been able to penetrate the polymeric network and affected the developed membrane potential. This effect is more pronounced when TAEAB is the added ion exchanger. Interestingly the inclusion of solvent mediators within the membrane composition did not significantly improve the selectivity coefficients. In certain cases such as when HCO_3^- was the interferent, selectivity for nitrate was compromised by the presence of a mediator.

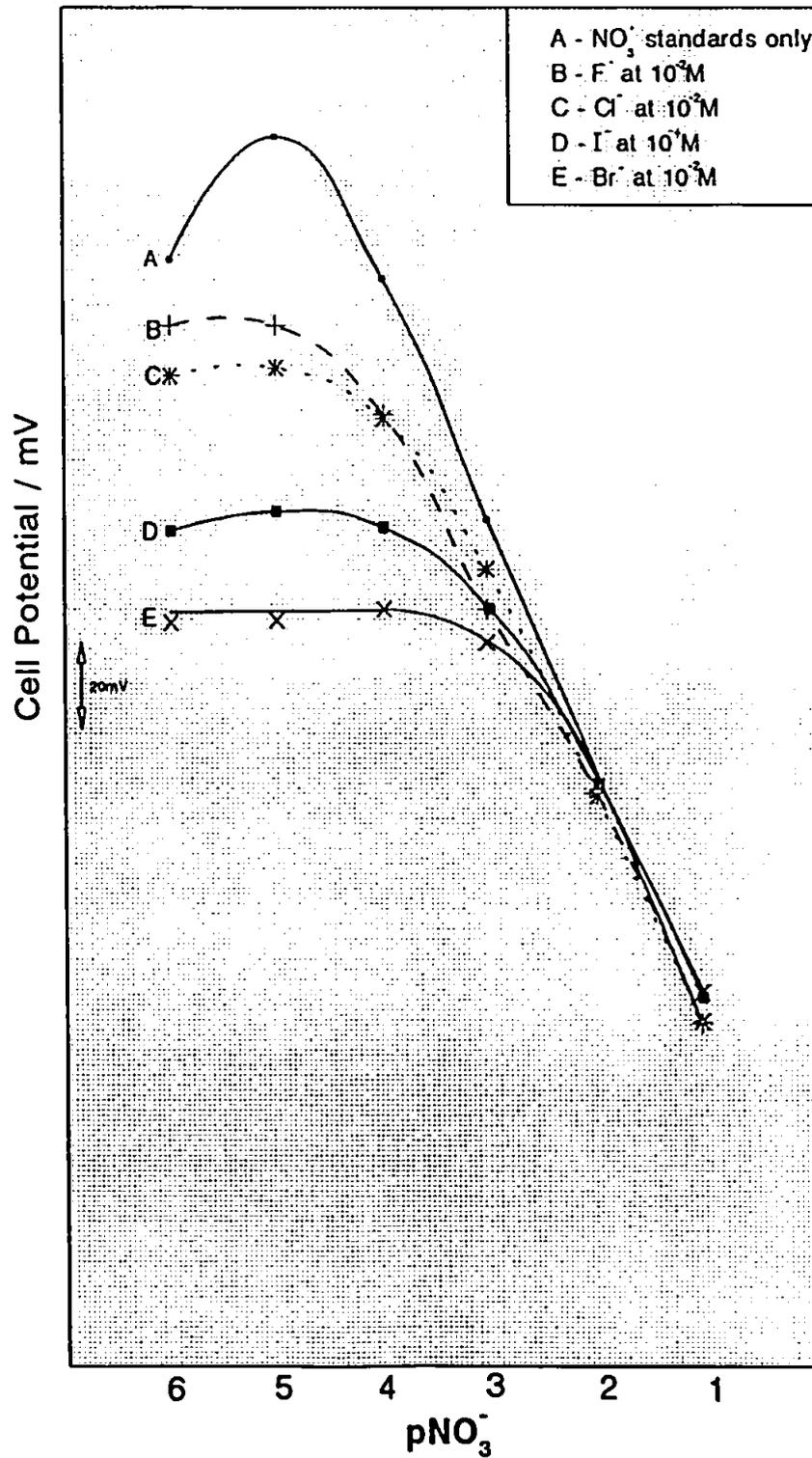
Membranes H10 and H12 fabricated with TABAB and either DBP or 2-NPOE as the solvent mediator produced the best electrodes. Calibration and selectivity data for membrane H12 is shown in Fig. 4.2

4.2.4 Membrane Lifetime Studies

Lifetime studies showed that sub-Nernstian slopes were obtained after only 2 months for membranes fabricated with nitrobenzene, DBP and solvent mediator free. The use of 2-NPOE as solvent mediator resulted in membranes with storage lifetimes of 4 months. This did not appear to be related to the immobilised sensor and therefore was presumably associated with the solvent mediator reducing the extraction of electroactive moieties by water.

Figure 4.2

Calibration and Selectivity Data for a Nitrate Selective Electrode using membrane H12



4.2.5 Cross-link Density Determinations

The cross-link density was determined by solvent swelling and certain EMK extracted membranes were evaluated for nitrate response. Cross-link density values are shown in Table 4.9.

Table 4.9

Nitrate Electrode Response and Cross-link Density Values for NBr Membranes

Membrane Number	Cross-link Density/mol cross-links cm^{-3}	EMK Extracted Slope/mV decade ⁻¹	Composition Notes
H1	1.3×10^{-5}	-	TABAB TBHP
H4	0.11×10^{-5}	-	TABAB TBHP DBP
H10	1.9×10^{-5}	-42.3(-59.0)*	TABAB DCP DBP
H12	1.7×10^{-5}	-42.0(-57.9)	TABAB DCP 2-NPOE
H13	1.4×10^{-5}	-	TABAB DCP nitrobenzene
H17	8.1×10^{-5}	-43.7(-58.9)	TABAB DCP none
H18	4.8×10^{-5}	-27.9(-58.1)	TAEAB DCP none
H19	2.4×10^{-5}	-	TAEAB DCP nitrobenzene
H20	1.8×10^{-5}	torn	TAEAB DCP DBP
H21	0.2×10^{-5}	-27.5(-57.9)	TAEAB DCP 2-NPOE

*Original results in parenthesis

The cross-link density values show the improvement in moving from TBHP to DCP, a more established organic peroxide widely used in the rubber industry. Dicumyl peroxide resulted in an increase in cross-links from 1.3×10^{-5} to a value of 8.1×10^{-5}

mol cross-links cm^{-3} for the solvent mediator free membrane. The introduction of diluents can affect the interpretation of results since intra-molecular links will be increased. The data demonstrated that a diluent caused a reduction in effective cross-links. The QAS appeared to have a significant effect on the cross-link formation since TABAB resulted in more links than TAEAB. This may have resulted in a higher level of covalently bound QAS and is partly supported by the response data for the EMK membranes. TABAB based membranes retained a far higher level of their original response following extraction than the TAEAB membranes. This may be due to extraction of uncross-linked TAEAB or alternatively to the easier removal of electroactive moieties in the polymer. It is possible that covalent attachment of QAS could result without the formation of a polymer-polymer cross-link. These would be analogous to termination reactions resulting from a polymer chain radical and QAS radical. This would not contribute to the effective cross-link density but would achieve the objective of covalently bonding the QAS groups. Therefore measurements of cross-link density can not be directly related to QAS covalent attachment.

4.3 Medium ACN Content NBr Membranes

4.3.1 Composition

The covalent attachment of the QAS with the polymer relied on reaction with the rubbery butadiene segment. Because of this, it was decided to utilise a polymer containing a higher proportion of butadiene. A medium ACN content nitrile rubber was evaluated. Membranes were fabricated using TAEAB and TABAB as the added ion exchanger. The solvent mediators 2-NPOE and DBP were selected for further

evaluation based on the results found using the high ACN content NBr polymer in Section 4.2. The composition of the membranes are shown in Table 4.10, and where a solvent mediator was used, a level of 40% m/m was selected.

Table 4.10

Composition of Medium ACN Content NBr Membranes

Membrane Number	TAEAB/ %m/m (pphr)	TABAB/ %m/m (pphr)	DCP/ %m/m (pphr)	Solvent Mediator
H22	-	-	13.4 (15.5)	none
H23	-	9.3 (11.9)	12.2 (15.5)	none
H24	-	5.6 (11.9)	7.3 (15.5)	DBP
H25	-	5.6 (11.9)	7.3 (15.5)	2-NPOE
H26	3.1 (10.2)	-	12.3 (15.5)	none
H27	4.9 (10.2)	-	7.4 (15.5)	DBP
H28	4.9 (10.2)	-	7.4 (15.5)	2-NPOE

4.3.2 Electrode Response

The electrode response of the hot pressed medium ACN membranes were evaluated in potassium nitrate standards containing potassium dihydrogen phosphate (10^{-2}M) as an ISAB. The selectivity co-efficient $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ was determined using the mixed solutions method and a constant intereferent of potassium chloride (10^{-1}M) was used. It was considered necessary to increase the level of interferent from 10^{-2}M potassium chloride because of the excellent selectivity for nitrate exhibited by the medium ACN NBr membranes. Results are shown in Table 4.11

Table 4.11

Nitrate Electrode Response for Medium ACN Content NBr Membranes

Membrane Number	Slope/mV decade ⁻¹	Limit of Detection/M	$k_{NO_3^-, Cl^-}^{pot}$	Composition Notes
H22	-8.3	-	-	NBr
H23	-33.6	-	-	TABAB none
H24	-57.7	3×10^{-5}	3.2×10^{-3}	TABAB DBP
H25	-57.5	4×10^{-5}	3.2×10^{-3}	TABAB 2-NPOE
H26	-12.6	-	-	TAEAB none
H27	-56.3	4×10^{-5}	2.0×10^{-3}	TAEAB DBP
H28	-56.6	1×10^{-4}	4.2×10^{-3}	TAEAB 2-NPOE

The omission of solvent mediator from the membrane composition for H23 and H26 had produced electrodes with a sub-Nernstian response to nitrate solutions in the range -33 to -12.6 mV decade⁻¹. The membranes which gave a Nernstian response also showed an improvement in selectivity. The use of medium ACN NBr as the membrane matrix improved the $k_{NO_3^-, Cl^-}^{pot}$ value from 10^{-2} to 3.2×10^{-3} . Interestingly it was the choice of polymer matrix which had affected the selectivity rather than choice of solvent mediator.

4.3.3 Selectivity Coefficient

Membrane H25 fabricated with TABAB and 2-NPOE was selected for evaluation for

$k_{NO_3^-, X^-}^{pot}$ and $k_{NO_3^-, X^{2-}}^{pot}$ for a range of anions (X^- and X^{2-}). The mixed solutions method was used. The sodium or potassium salt of the anion was added at a constant level as indicated in Table 4.12. A comparison was made with a commercial PVC nitrate ISE (Philips) and the best electrode for selectivity and lifetime from the work in Section 4.2.

Table 4.12

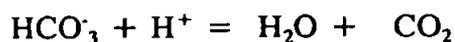
Nitrate Electrode Selectivity Data

Anion X Conc./M (for H25)	$k_{NO_3^-, X^-}^{pot}$ or $k_{NO_3^-, X^{2-}}^{pot}$		
	Membrane H12	Membrane H25	Commercial Membrane
F ⁻ (10 ⁻²)	1.9 x 10 ⁻³	7 x 10 ⁻³	10 ⁻⁴
Cl ⁻ (10 ⁻¹)	1.2 x 10 ⁻²	3.2 x 10 ⁻³	10 ⁻²
Br ⁻ (10 ⁻²)	8.9 x 10 ⁻²	5.0 x 10 ⁻²	0.3
I ⁻ (10 ⁻²)	2.5	4	10
SCN ⁻ (10 ⁻⁴)	15	7.9	40
ClO ₄ ⁻ (10 ⁻⁴)	1.2	14.1*	600
MnO ₄ ⁻ (10 ⁻⁶)	60	126	6.3
HCO ₃ ⁻ (10 ⁻⁴)	1.1 x 10 ⁻²	0.5	4 X 10 ⁻⁴
NO ₂ ⁻ (10 ⁻²)	7.9 x 10 ⁻²	9.0 x 10 ⁻²	5 x 10 ⁻²
SO ₄ ²⁻ (10 ⁻¹)	7.1 x 10 ⁻⁴	1.6 x 10 ⁻³	10 ⁻⁴

* Intercept method used

Membranes H12 and H25 showed a similar selectivity coefficient for a range of common anions. When chloride was the interferent, membrane H25 was far superior both to H12 and the commercial electrode. Both H12 and H25 were better than the

commercial electrode when perchlorate was the interferent. The reverse was true when hydrogen carbonate was the interferent. This was however not regarded as a limitation for the covalently bound QAS electrodes. It is possible to pretreat a given sample with a small volume of sulphuric acid to neutralise the hydrogen carbonate as shown below:



4.3.4 Membrane Lifetime Studies

The lifetime data was obtained for membrane H23 by determining the slope and limit of detection in potassium nitrate solutions containing potassium dihydrogen phosphate (10^{-2}M) as an ISAB. Results are shown in Table 4.13.

Table 4.13

Lifetime Data for a Nitrate Selective Electrode with Membrane H25

Time/day	Slope/mV decade ⁻¹	Limit of Detection/M
Original	-57.5	4×10^{-5}
21	-49.4	1×10^{-4}
58	-47.8	1.6×10^{-4}
105	-46.9	5.0×10^{-4}

The response for the membrane H25 became sub-Nernstian within 3 weeks of storage in 10^{-1}M potassium nitrate solution. The response then remained reasonably steady for the next 2½ months falling only to -46mV decade^{-1} . The effect upon the detection limit was more severe with a loss of an order of magnitude in sensitivity, falling to $5.0 \times 10^{-4}\text{M}$ nitrate.

4.3.5 Cross-link Density Determinations

The cross-link density was again determined by solvent swelling with EMK. The solvent was known to extract the solvent mediator during the swelling process. Because of this, none of the membranes exhibited permselectivity after extraction. The determined cross-link density values are shown in Table 4.14.

Table 4.14

Cross-link Density Values for Medium ACN Content NBr Membranes

Membrane Number	Cross-link Density/mol cross-links cm ⁻³
H22	46.6 x 10 ⁻⁵
H23	11.5 x 10 ⁻⁵
H24	2.6 x 10 ⁻⁵
H25	1.8 x 10 ⁻⁵
H26	11.8 x 10 ⁻⁵
H27	3.5 x 10 ⁻⁵
H28	1.8 x 10 ⁻⁵

4.4 Low ACN Content NBr Membranes

4.4.1 Composition

The use of a low ACN NBr polymer (19% ACN content) was evaluated with the expectation that an increased level of butadiene would facilitate greater covalent attachment of QAS groups. A reduced level of ACN was also expected to result in a lower level of absorbed water. This may reduce the tendency for solvent mediator and

electroactive moieties to be leached from the membrane surface. Both these factors were expected to play an important role in improving the membrane lifetime.

It was found that the use of 65% m/m of solvent mediator yielded membranes with poor physical strength. There was a pronounced tendency to either split or tear in use. The membranes had adequate strength for evaluation but lacked the robustness necessary for routine use. Membranes were fabricated with 40% m/m of solvent mediator which was deemed sufficient to allow normal handling. The composition of the membranes are shown in Table 4.15.

Table 4.15

Composition of Low ACN Content NBR Membranes

Membrane Number	TAEAB/ %m/m (pphr)	TABAB/ % m/m (pphr)	DCP/ % m/m (pphr)	Solvent Mediator/ %m/m (pphr)
H29	-	-	13.4 (15.5)	none
H30	-	9.3 (11.9)	12.2 (15.5)	none
H31	-	5.6 (11.9)	7.3 (15.5)	DBP (64.7, 233.4)
H32	-	5.6 (11.9)	7.3 (15.5)	2-NPOE (64.7, 233.4)
H33	8.1 (10.2)	-	12.3 (15.5)	none
H34	4.9 (10.2)	-	7.4 (15.5)	DBP (64.7, 233.4)
H35	4.9 (10.2)	-	7.4 (15.5)	2-NPOE (64.7, 233.4)
H36	-	6.6 (11.9)	8.5 (15.5)	DBP (40.0, 83.8)
H37	-	6.6 (11.9)	8.5 (15.5)	2-NPOE (40.0, 83.8)
H38	5.7 (10.2)	-	8.6 (15.5)	DBP (40.0, 83.8)
H39	5.7 (10.2)	-	8.6 (15.5)	2-NPOE (40.0, 83.8)

4.4.2 Electrode Response

The electrode response of the membranes was evaluated in potassium nitrate standards with potassium dihydrogen phosphate (10^{-2}M) added as an ionic strength adjustment buffer. The selectivity coefficient $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ was determined using the mixed solutions method. A constant level of 10^{-1}M potassium chloride was used. Results are shown in Table 4.16.

The omission of solvent mediator in membranes H30 and H33 resulted in sub-Nernstian responses. The reduction of DBP to 40% m/m for membranes H36 and H38 also produced a sub-Nernstian response. Interestingly, the use of 2-NPOE at the same level for the membranes H37 and H39, did not affect the electrode response. This would suggest that membranes incorporating 2-NPOE would maintain a normal response despite some extraction of the solvent mediator. The $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ values for the membranes based on 2-NPOE gave a superior selectivity for nitrate. This was an order of magnitude better than that obtained with either the 50% ACN content NBr membranes or the commercially available PVC nitrate ISE.

4.4.3 Selectivity Coefficients

Membrane H32 fabricated with TABAB and 2-NPOE was selected for evaluation for $k_{\text{NO}_3^-, \text{X}^-}^{\text{pot}}$ or $k_{\text{NO}_3^-, \text{X}^{2-}}^{\text{pot}}$ with a range of anions (X^- and X^{2-}). The mixed solutions method was used. Results are shown in Table 4.17 and are compared to the commercial electrode and the best NBr membrane, H25, based on 34% ACN NBr, TABAB and 2-NPOE.

Table 4.16

Nitrate Electrode Response for Low ACN Content NBr Membranes

Membrane Number	Slope/mV decade ⁻¹	Limit of Detection/M	$k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$	Composition Notes
H29	unresponsive	-	-	NBr
H30	-9.6	-	-	TABAB No mediator
H31	-58.6	4×10^{-5}	1.3×10^{-3}	TABAB DBP
H32	-58.1	2×10^{-5}	1.1×10^{-3}	TABAB 2-NPOE
H33	-33.0	-	-	TAEAB No mediator
H34	-57.0	7.9×10^{-5}	2.0×10^{-3}	TAEAB DBP
H35	-59.2	6.3×10^{-5}	1.3×10^{-3}	TAEAB 2-NPOE
H36	-38.2	-	-	TABAB low DBP
H37	-59.2	2.0×10^{-5}	1.9×10^{-3}	TABAB low 2-NPOE
H38	-26.6	-	-	TAEAB low DBP
H39	-59.0	2×10^{-5}	2.1×10^{-3}	TAEAB low 2-NPOE

Table 4.17

Nitrate Electrode Selectivity Data

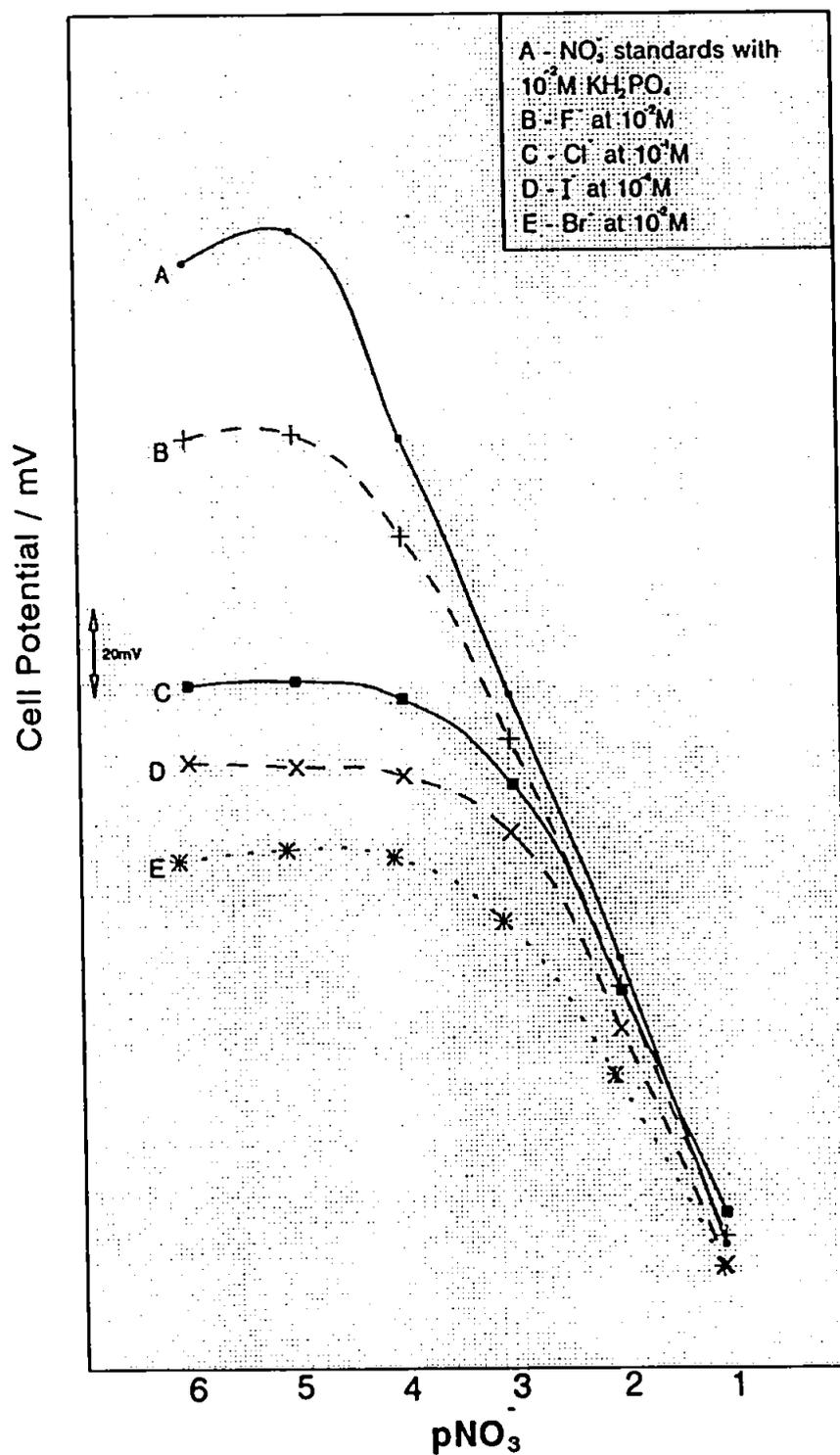
Anion X Conc ₀ /M (for H32)	$k_{NO_3^-, X^-}^{pot}$ and $k_{NO_3^-, X^{2-}}^{pot}$		
	Membrane H25	Membrane H32	Commercial Electrode
F ⁻ (10 ⁻²)	7 x 10 ⁻³	4 x 10 ⁻³	10 ⁻⁴
Cl ⁻ (10 ⁻¹)	3.2 x 10 ⁻³	1.1 x 10 ⁻³	10 ⁻²
Br ⁻ (10 ⁻²)	5.0 x 10 ⁻²	5.4 x 10 ⁻²	0.3
I ⁻ (10 ⁻⁴)	4	7	10
SCN ⁻ (10 ⁻⁴)	7.9	6.3	40
ClO ₄ ⁻ (10 ⁻⁴)	14.1*	7.9*	600
MnO ₄ ⁻ (10 ⁻⁶)	126	12.6	63
HCO ₃ ⁻ (10 ⁻⁴)	0.5	2	4 x 10 ⁻⁴
NO ₂ ⁻ (10 ⁻²)	9.0 x 10 ⁻²	7.0 x 10 ⁻²	5 x 10 ⁻²
SO ₄ ²⁻ (10 ⁻¹)	1.6 x 10 ⁻³	3.2 x 10 ⁻³	10 ⁻⁴

* Intercept method used

Membrane H32 had superior selectivity to both membranes H25 and the commercial electrode when chloride, permanganate and perchlorate were the interfering anions. Bicarbonate anions were a serious interferent for the NBr membranes compared to the commercial electrode. Calibration and selectivity data for membrane H32 is shown in Fig. 4.3.

Figure 4.3

Calibration and Selectivity Data for a Nitrate Selective Electrode using Membrane H32



4.4.4 Membrane Lifetime Studies

The lifetime data was obtained for membrane H32 by determination of the slope and limit of detection in potassium nitrate standards containing potassium dihydrogen phosphate (10^{-2}M) as an ISAB. Results are shown in Table 4.18:

Table 4.18

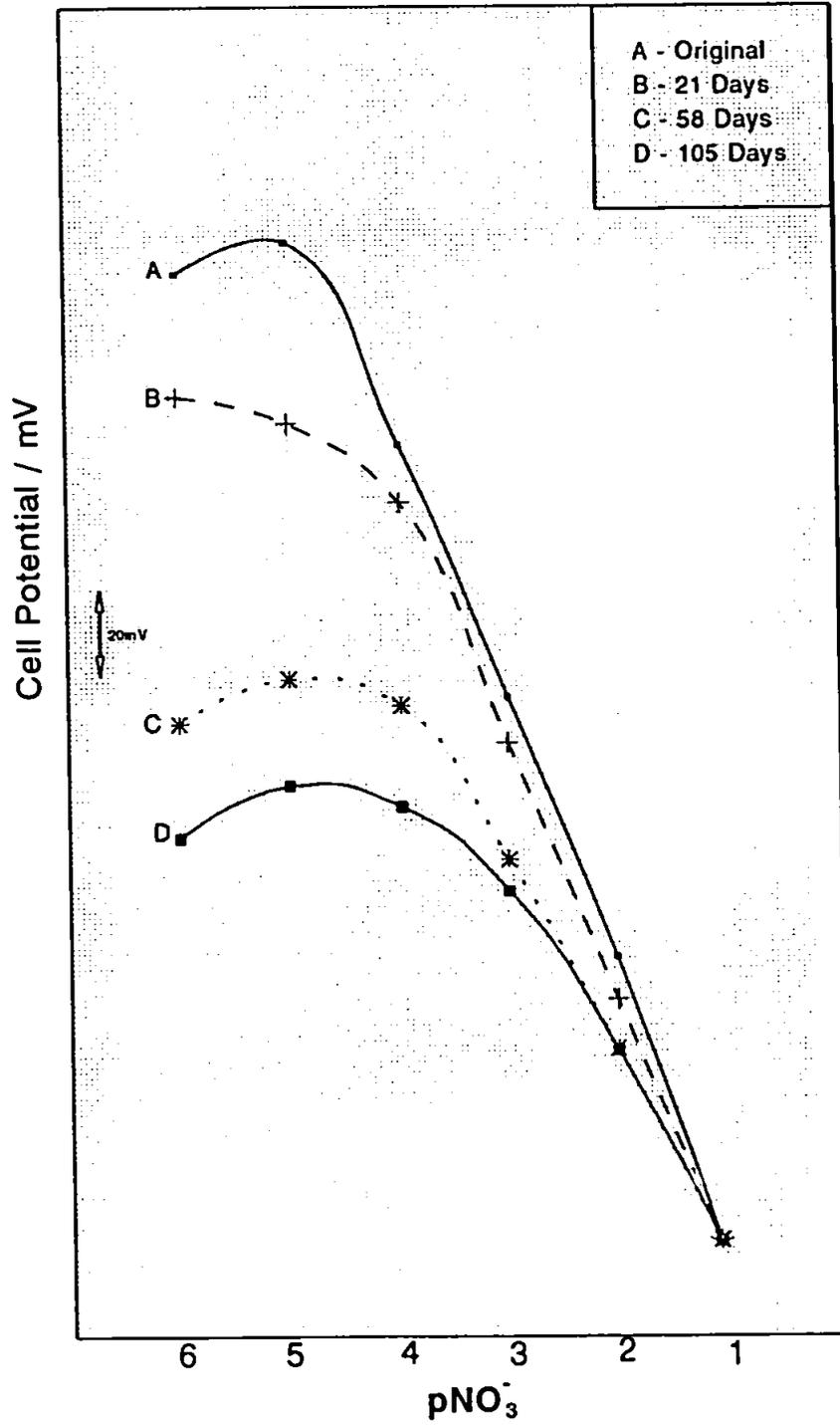
Lifetime Data for a Nitrate Slective Electrode With Membrane H32

Time/days	Slope/mV decade ⁻¹	Limit of Detection/M
Original	-58.1	2.0×10^{-5}
21	-57.6	4.5×10^{-5}
58	-44.2	1.3×10^{-4}
105	-40.3	4.0×10^{-4}

Membrane H32 had poor lifetime properties producing sub-Nernstian response within 2 months. Calibration curves produced over a 100 day period are shown in Fig. 4.4 for membranes stored in potassium nitrate solution (10^{-1}M).

Figure 4.4

Lifetime Study for a Nitrate Selective Electrode With Membrane H32



4.5 Effect of Cross-link Density on Electrode Response

4.5.1 Composition and Electrode Response

A range of membranes were fabricated based on H32 using TABAB and 2-NPOE. The level of initiator DCP was varied from relatively low to high values within the range 2.8% m/m to 10.4% m/m. The electrode response and cross-link density values were determined and these results together with DCP level are shown in Table 4.19. There was no relationship between DCP level, electrode response and $k_{NO_3^-, Cl^-}^{pot}$ within the range 2.8% m/m to 10.4% m/m. The membranes produced had cross-link density values ranging from 0.6×10^{-5} to 11.0×10^{-5} mol cross-links cm^3 . There was some suggestion that limit of detection data identified an optimum cross-link density but the results were inconclusive.

A plot of cross-link density against pphr of DCP added to the membrane is shown in Fig. 4.5. It can be seen that a relationship exists between the two properties. The curvature exhibited in Fig. 4.5 may be due to side reactions or possibly a level of 'quenching' of the free radical initiator. The polymer was purified before use in order to remove antioxidants which could behave as free radical scavengers. Incomplete removal of these additives could account for the observed results. The use of the 19% ACN polymer has, as predicted, resulted in an increase in cross-link density compared to the use of the 50% ACN polymer. This can be illustrated by comparing the cross-link density values for membrane H12 (50% ACN) 1.7×10^{-5} mol cross-links cm^{-3} to that of H32 3.8×10^{-5} mol cross-links cm^{-3} . The higher level of rubbery butadiene segments are expected to account for the observed results. If the increased cross-link density had resulted in a higher level of covalently bound QAS then longer membrane lifetimes would be expected.

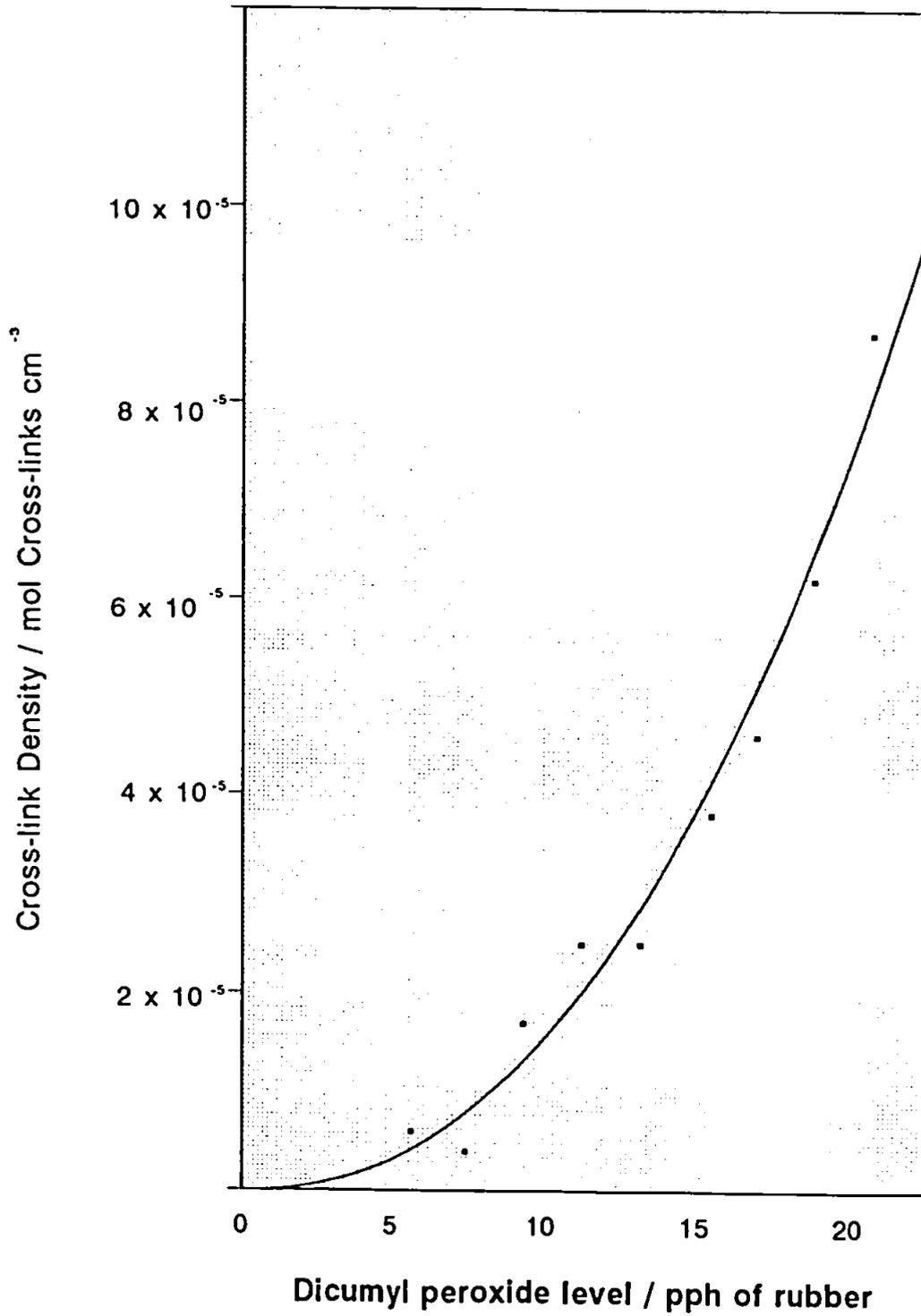
Table 4.19

Composition and Nitrate Electrode Response for Membranes with Varying Cross-link Density

Membrane Number	DCP/ % m/m (pphr)	Slope/mV decade ⁻¹	Limit of detection/M	$k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$	Cross-link density/mol cross-link cm ⁻³
H40	2.8 (5.7)	-56.1	1.1×10^{-4}	2.2×10^{-3}	0.6×10^{-5}
H41	3.7 (7.5)	-58.8	5×10^{-5}	2.2×10^{-3}	0.4×10^{-5}
H42	4.6 (9.4)	-59.2	7×10^{-5}	1.4×10^{-3}	1.7×10^{-5}
H43	5.4 (11.3)	-59.1	4.2×10^{-5}	2.5×10^{-3}	2.5×10^{-5}
H44	6.3 (13.2)	-59.1	2.5×10^{-5}	2.5×10^{-3}	3.0×10^{-5}
H32	7.3 (15.5)	-58.1	2.0×10^{-5}	1.1×10^{-3}	3.8×10^{-5}
H45	8.0 (17.0)	-57.1	6.3×10^{-5}	2.0×10^{-3}	4.6×10^{-5}
H46	8.8 (18.9)	-58.7	6.6×10^{-5}	2.0×10^{-3}	6.2×10^{-5}
H47	9.6 (20.8)	-58.1	2.0×10^{-5}	1.0×10^{-3}	8.7×10^{-5}
H48	10.4 (22.6)	-57.1	7.1×10^{-5}	1.3×10^{-3}	11.0×10^{-5}

Figure 4.5

Plot of Cross-link Density vs Dicumyl Peroxide Addition for Low ACN Content NBr Membranes



4.5.2 Membrane Lifetime Studies

Lifetime data was obtained for membrane H41 and H47 by measurement in potassium nitrate standards containing 10^{-2}M KH_2PO_4 as an ISAB. These membranes represented a low and high cross-link density respectively. Results are shown in Table 4.20

Table 4.20

Lifetime Data for Nitrate Selective Electrodes using Membranes H41 and H47

Time/day	H41 Slope/mV decade ⁻¹	H41 Limit of detection/M	H47 Slope/mV decade ⁻¹	H47 Limit of detection/M
Original	-58.8	5×10^{-5}	-58.1	2×10^{-5}
21	-58.7	6.3×10^{-5}	-59.1	6.3×10^{-5}
58	-47.4	3.2×10^{-4}	-44.5	2.5×10^{-4}
105	-34.1	1.0×10^{-3}	-37.8	7.9×10^{-4}

After only two months, sub-Nernstian responses had occurred for both the high and low cross-link density membranes. This would suggest that the increased number of cross-links had not resulted in increased covalent attachment of the QAS. It is postulated that the increased cross-linking has resulted from butadiene - butadiene cross-links and not butadiene - QAS - butadiene links. The results suggested that the electrochemical response may be based on a fixed site mechanism rather than a mobile ion exchanger. If this were not the case, we would have expected the high level of cross-links to have restricted mobility and consequently affected the membrane response.

4.5.3 Selectivity Coefficients

The response of Membranes H41 and H47 to a range of common interferents was investigated. Results are shown in Table 4.21.

Table 4.21

Nitrate Electrode Selectivity Data for High and Low Cross-link Density Membranes

Anion X Conc _a /M	$k_{NO_3^-, X^-}^{pot}$ and $k_{NO_3^-, X^{2-}}^{pot}$		
	Membrane H41	Membrane H47	Commercial electrode
F ⁻ (10 ⁻²)	6.3 x 10 ⁻²	6.3 x 10 ⁻³	10 ⁻⁴
Cl ⁻ (10 ⁻¹)	2.2 x 10 ⁻³	1.0 x 10 ⁻³	10 ⁻²
Br ⁻ (10 ⁻²)	8.0 x 10 ⁻²	9.0 x 10 ⁻²	0.3
I ⁻ (10 ⁻⁴)	5	7.9	10
SCN ⁻ (10 ⁻⁴)	15.8	6.3	40
ClO ₄ ⁻ (10 ⁻⁴)	15.8*	22.4*	600
MnO ₄ ⁻ (10 ⁻⁶)	100	40	63
HCO ₃ ⁻ (10 ⁻⁴)	10	5	4 x 10 ⁻⁴
NO ₂ ⁻ (10 ⁻²)	7.9 x 10 ⁻²	7.9 x 10 ⁻²	5 x 10 ⁻²
SO ₄ ²⁻ (10 ⁻¹)	4.0 x 10 ⁻³	2.0 x 10 ⁻³	10 ⁻⁴

* Intercept method used

There is little difference between the selectivity coefficients for the two membranes. This would support other data which showed that cross-link density does not affect electrode performance.

The only significant difference occurred when the small fluoride anion was the interferent. The high cross-link density membrane H47 is superior and this may be due to restricted access to the fluoride anion. It is possible that the extensive 3 dimensional network restricts the entry of the anion into the matrix and hence reduced the level of interference. This effect is not observed with the other anions tested and the Hofmeister selectivity series was maintained.

CHAPTER 5

New Ion Exchangers and Polymer Matrices

5.1 Membranes Fabricated with Triallyloctylammonium Bromide

5.1.1 Composition

Earlier work in section 3.2.2 had shown a difference in the selectivity coefficients between the ion exchangers triallyethylammonium bromide (TAEAB) and triallylbutylammonium bromide (TABAB). Based on the $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ values for the ethyl and butyl derivatives, it was hoped that increasing the length of the alkyl group would further enhance selectivity coefficients. In addition longer alkyl chains would replicate the ion exchangers used in commercial PVC based nitrate ion selective electrodes (ISEs). These use QASs such as tetraoctylammonium nitrate (Corning and Philips) and tetradodecylammonium nitrate (EIL) [117]. The increase in alkyl chain length was predicted to increase hydrophobicity. The immobilisation reaction should not be influenced by an increase in alkyl chain length since the availability of the reactive allyl groups remains unchanged.

Triallyloctylammonium bromide TAOAB was a very hygroscopic powder. During the membrane fabrication process it was weighed quickly to prevent moisture absorption. The composition of the membranes are shown in Table 5.1. These included the use of 19, 34, and 50% acrylonitrile (ACN) content poly(acrylonitrile-butadiene) (NBr) and solvent mediator 2-nitrophenyl octyl ether (2-NPOE) in membranes H63, H65 and H66. Membranes H67 and H68 based on the 19% ACN content polymer (Krynac 19.50) were also fabricated using high (9.4% m/m) and low (3.6% m/m) levels of dicumyl peroxide (DCP).

Table 5.1

Composition of Membranes Fabricated with Triallyloctylammonium Bromide

Membrane Number	Polymer/ % ACN	TAOAB/% m/m (pphr)	DCP/% m/m (pphr)	Solvent Mediator/% m/m pphr)
H60	50	10.8 (14.0)	12.0(15.5)	-
H61	50	-	13.4(15.5)	-
H62	50	12.3 (14.0)	-	-
H63	50	6.5 (14.0)	7.2 (15.5)	2 NPOE 39.7, (84.9)
H64	50	6.5 (14.0)	7.2 (15.5)	DBP 39.7, (84.9)
H65	34	6.5 (14.0)	7.2 (15.5)	2 NPOE 39.7, (84.9)
H66	19	6.5 (14.0)	7.2 (15.5)	2 NPOE 39.7, (84.9)
H67	19	6.7 (14.0)	3.6 (7.5)	2 NPOE 41.2, (84.9)
H68	19	6.4 (14.0)	9.4 (20.8)	2 NPOE 38.8, (84.9)

5.1.2 Electrode Response

Discs 7mm in diameter were punched from the master membranes and conditioned in potassium nitrate solution ($10^{-1}M$) for 7 days. After conditioning, the membranes were tested for response toward potassium nitrate standards containing potassium dihydrogen phosphate ($10^{-2}M$) as the ionic strength adjustment buffer (ISAB). The electrochemical response for membranes H60 to H68 are shown in Table 5.2.

Table 5.2

Nitrate Electrode Response of Triallyloctylammonium Bromide Membranes

Membrane Number	Slope/mV decade ⁻¹	Limit of Detection/M	$k_{NO_3^-,Cl^-}^{pot}$
H60	-55.3	2.5×10^{-5}	2.2×10^{-3}
H61	unresponsive	-	-
H62	-58.4	2.5×10^{-5}	5.9×10^{-3}
H63	-58.3	4.5×10^{-5}	5.3×10^{-3}
H64	-58.6	5.0×10^{-5}	6.3×10^{-3}
H65	-58.8	3.5×10^{-5}	2.1×10^{-3}
H66	-58.6	2.5×10^{-5}	2.1×10^{-3}
H67	-59.2	3.5×10^{-5}	1.8×10^{-3}
H68	-58.6	2.0×10^{-5}	1.8×10^{-3}

All of the electrodes gave a Nernstian response except for H61 fabricated without the addition of the ion exchanger TAOAB. The $k_{NO_3^-,Cl^-}^{pot}$ selectivity values were all superior to a commercially available PVC membrane electrode (Philips) which had a $k_{NO_3^-,Cl^-}^{pot}$ value of 1.2×10^{-2} . Reduction of the ACN content of the polymer gave an improvement in the selectivity coefficient. The limit of detection for the electrodes was not significantly affected by the various membrane compositions evaluated.

Comparison of the results for TAOAB based membranes to those recorded for both TAEAB and TABAB membranes showed differences only in selectivity. For all membranes similar limits of detection and Nernstian slope were obtained, but there

were differences in $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ values. The use of 34 and 19% ACN content NBr as the polymer matrix in membranes H65-H68 produced superior $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ values of between 1.8 and 2.1×10^{-3} compared to 50% ACN solvent mediated membranes H63 and H64 with $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ values of 5.3×10^{-3} and 6.3×10^{-3} respectively. Interestingly the 50% ACN content non-solvent mediator membrane H60 with immobilised QAS produced a $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ value of 2.2×10^{-3} . The use of TAOAB as the ion exchanger improved the $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ value for 50% ACN NBr matrix membranes compared to the use of either triallylethylammonium bromide (TAEAB) or triallylbutylammonium bromide (TABAB). These membranes reported in section 4.2.3 had $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ values of 2.0×10^{-2} (TAEAB) and 1.3×10^{-2} (TABAB). The use of 34 and 19% ACN content NBr as the membrane matrix with TAOAB did not show any improvements compared to the TAEAB and TABAB membranes reported in section 4.3.3 and 4.4.3.

5.1.3 Membrane Lifetime

Electrode lifetime was evaluated by storage of the individual membranes in the 10^{-1}M potassium nitrate conditioning solution. The electrode performance was determined periodically in potassium nitrate standards containing potassium dihydrogen phosphate (10^{-2}M) as the ISAB. Results for both slope and limit of detection are shown in Table 5.3.

Membrane H63 was clearly superior from a lifetime point of view and maintained a Nernstian response after more than 665 days. This membrane was fabricated with the 50% ACN content NBr, 2-NPOE, DCP and the TAOAB ion exchanger.

Table 5.3

Lifetime Studies for Nitrate Selective Electrodes with Triallyloctylammonium Bromide Membranes

Parameter	Membrane H60	Membrane H62	Membrane H63	Membrane H64	Membrane H65	Membrane H66	Membrane H67	Membrane H68
Original slope/mV decade ⁻¹	-55.3	-58.4	-58.3	-58.6	-58.6	-58.6	-59.2	58.6
Limit of Detection/M	2.5x10 ⁻⁵	2.5x10 ⁻⁵	4.5x10 ⁻⁵	2.5x10 ⁻⁵	2.5x10 ⁻⁵	2.5x10 ⁻⁵	2.5x10 ⁻⁵	2.5x10 ⁻⁵
21 Days slope/mV decade ⁻¹	-56.1	-51.8	-58.2	-57.5	-57.4	-58.7	-59.2	-59.1
Limit of Detection/M	7.9x10 ⁻⁵	1.3x10 ⁻⁴	6.3x10 ⁻⁵	7.9x10 ⁻⁵	1x10 ⁻⁴	1x10 ⁻⁴	1.3x10 ⁻⁴	7.9x10 ⁻⁵
58 Days slope/mV decade ⁻¹	-55.0	-49.7	-58.7	-59.0	-54.3	-58.5	-56.5	-56.8
Limit of Detection/M	5.0x10 ⁻⁵	8.9x10 ⁻⁵	7.0x10 ⁻⁵	5.0x10 ⁻⁵	6.3x10 ⁻⁵	7.0x10 ⁻⁵	8.9x10 ⁻⁵	8.9x10 ⁻⁵
106 Days slope/mV decade ⁻¹	-31.2	-42.5	-58.2	-16.5	-54.8	-41.6	-42.7	-55.8
Limit of Detection/M	5.0x10 ⁻⁴	4x10 ⁻⁴	4.0x10 ⁻⁵	1.6x10 ⁻⁴	6.3x10 ⁻⁵	3.2x10 ⁻⁴	6.3x10 ⁻⁵	5.0x10 ⁻⁵
139 Days slope/mV decade ⁻¹	-	-	-58.2	-	-55.9	-	-	-51.6
Limit of Detection/M	-	-	5.0x10 ⁻⁵	-	1x10 ⁻⁴	-	-	1.3x10 ⁻⁴
369 Days slope/mV decade ⁻¹	-	-	-58.2	-	-47.6	-	-	-33.2
Limit of Detection/M	-	-	7.0x10 ⁻⁵	-	2.15x10 ⁻⁴	-	-	-
412 Days slope/mV decade ⁻¹	-	-	-58.9	-	-	-	-	-
Limit of Detection/M	-	-	6.3x10 ⁻⁵	-	-	-	-	-
510 Days slope/mV decade ⁻¹	-	-	-58.2	-	-	-	-	-
Limit of Detection/M	-	-	6.3x10 ⁻⁵	-	-	-	-	-
665 Days slope/mV decade ⁻¹	-	-	-58.6	-	-	-	-	-
Limit of Detection/M	-	-	2x10 ⁻⁵	-	-	-	-	-

Omission of the solvent mediator in membrane H60 produced a sub-Nernstian response after 100 days storage. The use of DBP as the solvent mediator in membrane H64 also produced a sub-Nernstian response after 100 days. The use of TAOAB has as predicted resulted in extended membrane lifetimes.

The ACN content of the polymer played a significant role in determining the electrode lifetime as witnessed by the use of 50%, 34% and 19% ACN content polymers in membrane H63, H65 and H66. Sub-Nernstian responses occurred after 369 days and 106 days for membranes H65 and H66 respectively. Increasing the ACN content of the polymer gave longer membrane lifetime but poorer $k_{NO_3^-, Cl^-}^{pot}$ selectivity values. Conversely, reducing the ACN content gave shorter membrane lifetimes but superior $k_{NO_3^-, Cl^-}^{pot}$ values. The use of low (3.6% m/m) and high (9.4% m/m) levels of DCP in membranes H67 and H68 produced a difference in lifetime behaviour. After 100 days membrane H67 gave a sub-Nernstian response whereas H68 still displayed Nernstian behaviour. After 139 days membrane H68 also gave a sub Nernstian response. The difference was attributed to the extent of membrane cross-linking which had been shown in section 4.5 to be directly related to the level of DCP. Membrane H67 was fabricated with a low (3.6% m/m) level whilst H68 had a high (9.4% m/m) DCP level. This will have produced a higher cross-link density and the potential for more covalently bound QAS in membrane H68. These results could offer an additional approach to optimise further the membrane composition and extend electrode lifetime even beyond 665 days as reported for membrane H63.

5.2 Membranes Fabricated with Triallyldodecylammonium Bromide

5.2.1 Composition

The quaternary ammonium compound triallyldodecylammonium bromide (TADDAB) was a highly hygroscopic oily liquid which was very difficult to handle. The composition of the fabricated membranes are shown in Table 5.4. These included the use of the 50, 34 and 19% ACN polymer and the solvent mediators 2-NPOE and DBP. The effect of low (3.6% m/m) and high (9.3% m/m) levels of DCP were also investigated with the 19% ACN polymer.

Table 5.4

Composition of Membranes Fabricated with Triallyldodecylammonium Bromide

Membrane Number	Polymer /%ACN Content	TADDAB/ % m/m (pphr)	DCP/ % m/m (pphr)	Solvent Mediator/ % m/m (pphr)
H69	50	12.4 (16.4)	11.7 (15.5)	-
H70	50	14.1 (16.4)	-	-
H71	50	7.5 (16.4)	7.1 (15.5)	2-NPOE 39.3, (85.0)
H72	50	7.5 (16.4)	7.1 (15.5)	DBP 39.3, (85.0)
H73	34	7.5 (16.4)	7.1 (15.5)	2-NPOE 39.3, (85.0)
H74	19	7.5 (16.4)	7.1 (15.5)	2-NPOE 39.3, (85.0)
H75	19	7.9 (16.4)	3.6 (7.5)	2-NPOE 40.7, (85.0)
H76	19	7.4 (16.4)	9.3 (20.8)	2-NPOE 38.3, (85.0)

The membranes were fabricated as described previously. The resultant material was then hot pressed at 150°C for 10 minutes to effect cross-linking. The hot pressed membranes were found to be greasy to the touch. This may be due to poor

compatibility between the polymer and TADDAB, which on storage could result in migration to the surface of non-immobilised ion exchanger. The incompatibility could have arisen because of the increased alkyl chain length going from octyl to dodecyl. The increase in the length of the alkyl chain had previously resulted in a change from a solid (octyl derivative) to an oily liquid (dodecyl derivative) ion exchanger QAS.

5.2.2 Electrode Response

The electrochemical response for membranes H69 to H76 were determined in potassium nitrate solutions containing 10^{-2} M potassium dihydrogen phosphate as an ISAB. The $k_{NO_3^-, Cl^-}^{pot}$ selectivity coefficient was determined with the use of a constant interferent level of 10^{-1} M potassium chloride. Results are shown in Table 5.5 below:

Table 5.5

Nitrate Electrode Response for Triallyldodecylammonium Bromide Membranes

Membrane Number	slope/mV decade ⁻¹	Limit of Detection/ M	$k_{NO_3^-, Cl^-}^{pot}$
H69	-57.6	2.0×10^{-5}	7.1×10^{-3}
H70	-55.1	3.2×10^{-5}	1.0×10^{-2}
H71	-57.8	4.5×10^{-5}	6.3×10^{-3}
H72	-59.1	8.9×10^{-5}	8.9×10^{-3}
H73	-51.4	7.1×10^{-5}	5.6×10^{-3}
H74	-56.2	4.5×10^{-5}	6.3×10^{-3}
H75	-57.3	4.5×10^{-5}	3.2×10^{-3}
H76	-55.0	6.3×10^{-5}	3.5×10^{-3}

Membranes fabricated with TADDAB, all gave Nernstian responses except for membrane H73 which subsequently gave a Nernstian response on storage. The response for the TADDAB membranes were found to be more variable than previously

observed with the TAOAB membranes. The range of results may be attributed to the reduced compatibility between the polymer and TADDAB.

The $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ values were slightly inferior to those obtained using TAOAB as the added ion exchanger. They were however again superior to the value obtained from a commercially available PVC membrane nitrate selective electrode (Philips). These selectivity values did not follow the simple pattern of improving with reducing ACN content of the polymer as previously observed with the TAOAB membranes.

5.2.3 Membrane Lifetime

Electrode lifetime was determined by storage of the individual membranes in the conditioning solution and the electrochemical response was determined periodically. Results are shown in Table 5.6. The use of entrapped TADDAB in membrane H70 provided a long life membrane which maintained a Nernstian response for 230 days. The introduction of the crosslinking agent DCP in membrane H69 resulted in a short lifetime membrane which gave a sub-Nernstian response after 76 days. The long lifetime for membrane H70 which contained simply entrapped TADDAB could be explained by the increase in the alkyl chain length to the dodecyl derivative. This will have reduced the mobility of the entrapped ion exchanger within the polymeric membrane. It is postulated that as the ion exchanger was dissolved from the water-membrane interface, more ion exchanger diffused from the bulk membrane and in this way, a Nernstian response was maintained for a long period. The approach of entrapment is the same as that used in plasticised PVC membranes. In addition to extraction of the ion exchanger, PVC membranes have the additional problem of solvent mediator extraction which can also limit electrode lifetime [48]. The membrane

Table 5.6

Lifetime Studies for Nitrate Selective Electrodes with Triallyldodecylammonium Bromide Membranes

Parameter	Membrane H69	Membrane H70	Membrane H71	Membrane H72	Membrane H73	Membrane H74	Membrane H75	Membrane H76
Original slope/mV decade ⁻¹	-57.6	-55.1	-57.8	-59.1	-51.4	-56.2	-57.3	-55.0
Limit of Detection/M	2.0x10 ⁻⁵	3.2x10 ⁻⁵	4.5x10 ⁻⁵	8.9x10 ⁻⁵	7.1x10 ⁻⁵	4.5x10 ⁻⁵	4.5x10 ⁻⁵	6.3x10 ⁻⁵
76 Days slope/mV decade ⁻¹	-32.1	-54.9	-58.9	-59.5	-56.6	-54.9	-56.8	-56.5
Limit of Detection/M	4.4x10 ⁻⁵	7.9x10 ⁻⁵	1.3x10 ⁻⁴	8.9x10 ⁻⁵	1.3x10 ⁻⁴	8.9x10 ⁻⁵	1.0x10 ⁻⁴	1.0x10 ⁻⁴
131 Days slope/mV decade ⁻¹	-	-56.5	-56.7	-57.7	-53.9	-54.5	-55.7	-55.1
Limit of Detection/M	-	7.9x10 ⁻⁵	5.0x10 ⁻⁵	7.9x10 ⁻⁵	1.0x10 ⁻⁴	7.9x10 ⁻⁵	1.1x10 ⁻⁴	1.3x10 ⁻⁴
231 Days slope/mV decade ⁻¹	-	-57.6	-57.4	-29.3	-56.0	-57.7	-57.6	-56.3
Limit of Detection/M	-	5 x10 ⁻⁵	7.9x10 ⁻³	1.3x10 ⁻³	6.3x10 ⁻⁵	4.3x10 ⁻⁵	6.3x10 ⁻⁵	1.2x10 ⁻⁴
330 Days slope/mV decade ⁻¹	-	-51.0	-57.7	-	-57.6	-51.6	-56.9	-57.6
Limit of Detection/M	-	6.3x10 ⁻⁵	7.1x10 ⁻⁵	-	6.3x10 ⁻⁵	7.9x10 ⁻⁵	7.9x10 ⁻⁵	6.3x10 ⁻⁵
463 Days slope/mV decade ⁻¹	-	-12.6	-57.6	-	-57.3	-46.1	-53.4	-57.1
Limit of Detection/M	-	2.5x10 ⁻⁴	5.6x10 ⁻⁵	-	3.5x10 ⁻⁵	7.0x10 ⁻³	6.3x10 ⁻⁵	7x10 ⁻⁵

H70 containing the entrapped ion exchanger did not require a solvent mediator to form a functioning electrode.

The significant difference between the effect of 2-NPOE and DBP as solvent mediators was illustrated by membrane H71 and H72 respectively. The use of DBP resulted in a sub-Nernstian response after 230 days whilst 2-NPOE continued to give a Nernstian response after 463 days. Reduction of the ACN content of the polymer from 50% to 34% in membrane H73 also with the use of 2-NPOE gave long life membranes and a Nernstian response was obtained after 463 days of storage.

The use of 19% ACN content in membranes H74, H75 and H76 provided some interesting results. The use of the normal (7.1% m/m) level of DCP in membrane H74 gave a sub-Nernstian response after 330 days. This behaviour was similar to the properties displayed by the TAOAB membranes. The use of a 19% ACN polymer content was shown to reduce the membrane lifetime. The use of a low level (3.6% m/m) of DCP produced a membrane similar in behaviour to that of the entrapped membrane H70. These results indicated that there is an optimum level of crosslinking agent when TADDAB was the added ion exchanger. It is possible that the lower level of crosslinking agent enabled a greater degree of mobility for any of the non-immobilised ion exchanger. This suggestion would fit with the observation that the TADDAB membranes were greasy to the touch due to migration of non-immobilised ion exchanger. A high level (9.3% m/m) of DCP gave the longest 19% ACN polymer membrane lifetime with a Nernstian response maintained after 463 days.

5.3. Membranes Fabricated with Betaine as the Ion Exchanger

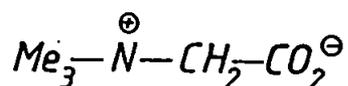
In this work so far quaternary ammonium compounds have been used as the ion exchanger. These were synthetic materials which were tailor made to be covalently bound within the polymeric matrix. There are a limited number of naturally occurring quaternary ammonium compounds. Betaine is one such compound which can be found in plants. It is found in high concentrations in those plants which are able to tolerate a high salt environment [113]. These plants are called halophytes and the resistance is due to one of three mechanisms:

- 1 accumulation of NaCl within the vacuole;
- 2 resistance to NaCl entry;
- 3 dilution of NaCl within the plant.

Two differences between halophytes and other plants are, accumulation of the protein imino acid proline and the quaternary ammonium compound glycine betaine [114]. In view of this observation, it was decided to investigate the suitability of glycine betaine as an ion exchanger within a polymeric ion selective electrode (ISE). The structure of betaine is shown below in fig 5.1

Figure 5.1

Glycine Betaine



Because of the lack of unsaturated groups clearly the immobilisation of glycine betaine within the polymer network by free radical initiated cross-linking was not possible. Membranes were however fabricated with the betaine entrapped within a crosslinked polymeric network.

Such membranes were not predicted to have the long lifetime displayed by the immobilised ion exchanger membranes. However, they offered the opportunity easily to assess a new range of ion exchangers. Further synthetic work would have been necessary to achieve immobilisation and was regarded as outside the scope of the present work.

5.3.1 Composition

The composition of the fabricated membranes are shown below in Table 5.7. The betaine (Sigma) and betaine hydrochloride (Sigma) were at the same mole % as the ion exchanger used previously. The 50% ACN content nitrile rubber was selected as the polymer matrix.

Table 5.7

Composition of Membranes Fabricated with Betaine as the Ion Exchanger

Membrane Number	Betaine/ % m/m (pphr)	Betaine hydrochloride / % m/m(pphr)	DCP/ % m/m (pphr)	Solvent Mediator / % m/m (pphr)
H77	2.4 (4.9)	-	7.5 (15.5)	2-NPOE (41.5, 85.2)
H78	-	3.1 (6.4)	7.5 (15.5)	2-NPOE (41.2, 85.2)
H79	4.1 (4.9)	-	12.8 (12.8)	None
H80	-	5.4 (6.5)	12.7 (12.7)	None

5.3.2 Electrode Response

Discs 7mm in diameter were punched from the membrane and conditioned in 10^{-1} M potassium nitrate. Electrode performance was evaluated as previously described and results are shown in Table 5.8.

Table 5.8

Nitrate Electrode Response for Membranes Containing Betaine

Membrane Number	Slope/mV decade ⁻¹	Limit of detection/M	$k_{NO_3^-, Cl^-}^{pot}$
H77	-51.3	2.8×10^{-4}	4.0×10^{-3}
H78	-52.5	4.5×10^{-4}	5.6×10^{-3}
H79	-19.9	-	-
H90	-16.2	-	-

After 50 days storage membrane H77 and H78 gave a slope of -47.8 and -47.9 mV decade⁻¹ respectively. These results showed that all four membranes gave sub-Nernstian responses. The presence of the solvent mediator was necessary to give a satisfactory response suitable for analytical determinations. The betaine based membranes gave rather poor limits of detection. This was attributed to the solubility of the betaine combined with only entrapment of the ion exchanger. The limit of detection is determined by a number of factors and, in this case, appeared to be limited by the solubility of betaine. The selectivity value $k_{NO_3^-, Cl^-}^{pot}$ was very good and comparable to the best electrodes tested in this work. It is interesting to speculate that the ability for plants to selectively take up nitrate in preference to chloride anions has been a driving force in the development of selectivity. The reduction in slope on

storage supports the suggestion of slow betaine dissolution from the membrane. These results are most encouraging and indicate that naturally occurring betaines are worthy of further work. If they could be successfully immobilised within a matrix, a novel sensor may be successfully developed.

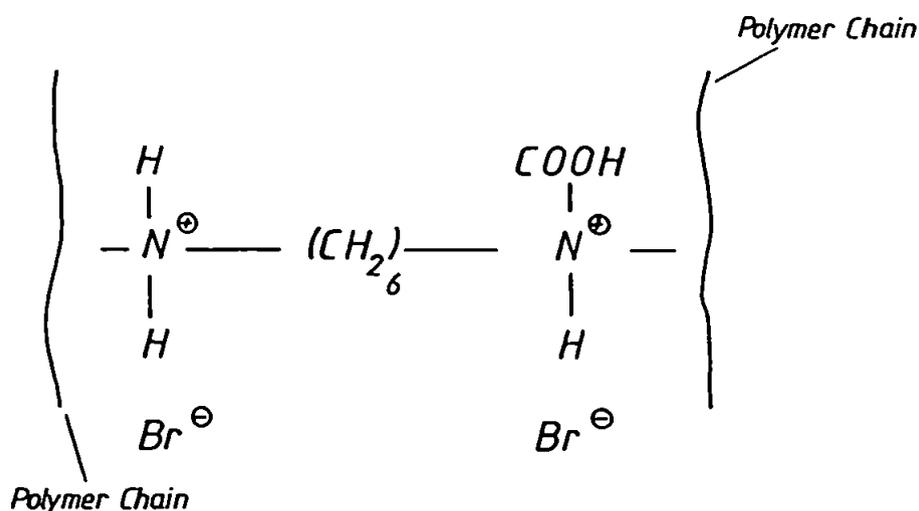
5.4 Bromobutyl Rubber Membranes

5.4.1 Composition

Diak No. 1 (Hexamethylenediamino-carbamate) (DuPont, Hemel Hempstead, UK) is a commonly used diamine in the vulcanisation of bromobutyl rubber. The expected cross-links are composed of two quaternary ammonium sites as shown in fig. 5.2

Figure 5.2

Proposed Cross-link for Bromobutyl Rubber Formed with Diak No. 1



The selected bromobutyl grade 2244 (Exxon UK Ltd, Fawley UK.) contained 2 mole % of bromine. Therefore, since 1 mole of diamine will react with 2 moles of bromine the theoretical addition would be 1 mole %. The Exxon handbook [91] recommended the use of 0.5 to 2.0 pphr. Membrane composition was as shown in Table 5.9.

Table 5.9

Composition of Bromobutyl Rubber Membranes

Membrane Number	Diak No. 1/% m/m (pphr)	Bromobutyl Rubber
81	0.5 (2.5)	Purified
82	2.0 (10)	Purified
83	0.5 (2.5)	As Received
84	2.0 (10)	As Received

An excess of diamine was used to ensure a maximum number of crosslinks and hence immobilised quaternary ammonium groups. The membranes were fabricated with the use of traditional rubber industry equipment rather than by solvent dissolution. The bromobutyl was softened and heated on a 6" diameter two roll mill (J. Robinson and Co. Ltd., Salford, UK). After 2 minutes the diamine was added to the polymer and incorporated into the mass. Good dispersion was achieved by passing the polymer through the mill nip 10 times. The ability of the rubber to cross-link was confirmed by the use of an oscillating disk rheometer (ODR) (Monsanto Rheometer 100, Monsanto UK, Swindon, UK).

The Monsanto Rheometer worked on the principle of enclosing a small disc within a heated mould. The force or torque to turn the disc through a 1, 3 or 5° arc was recorded against time.

An ideal rheological curve is shown in fig. 5.3. with 4 main phases as follows:

A sharp increase in torque as rubber is forced around disc;

- B reduction in torque reaching a minimum value ML as heat softened the rubber;
 - C increase in torque as cross-linking reaction commences. This is characterised by the so called scorch time determined by the ML value plus 2 pounds force (lbf);
 - D plateau as the cross-linking reaches a maximum value MH. The theoretical cure time can be calculated as the time to reach 90% of the maximum cross-links.
- The results for the 4 rubber mixes are shown in Table 5.10:

Table 5.10

Rheological data for Bromobutyl Rubber Membranes

Membrane Number	ML/lbf	Scorch Time/minute	MH/lbf	Cure time/minute
H81	5.5	2.1	10.6	4.8
H82	5.8	1.0	20.1	5.5
H83	6.0	2.0	10.4	4.5
H84	5.8	1.2	19.5	5.6

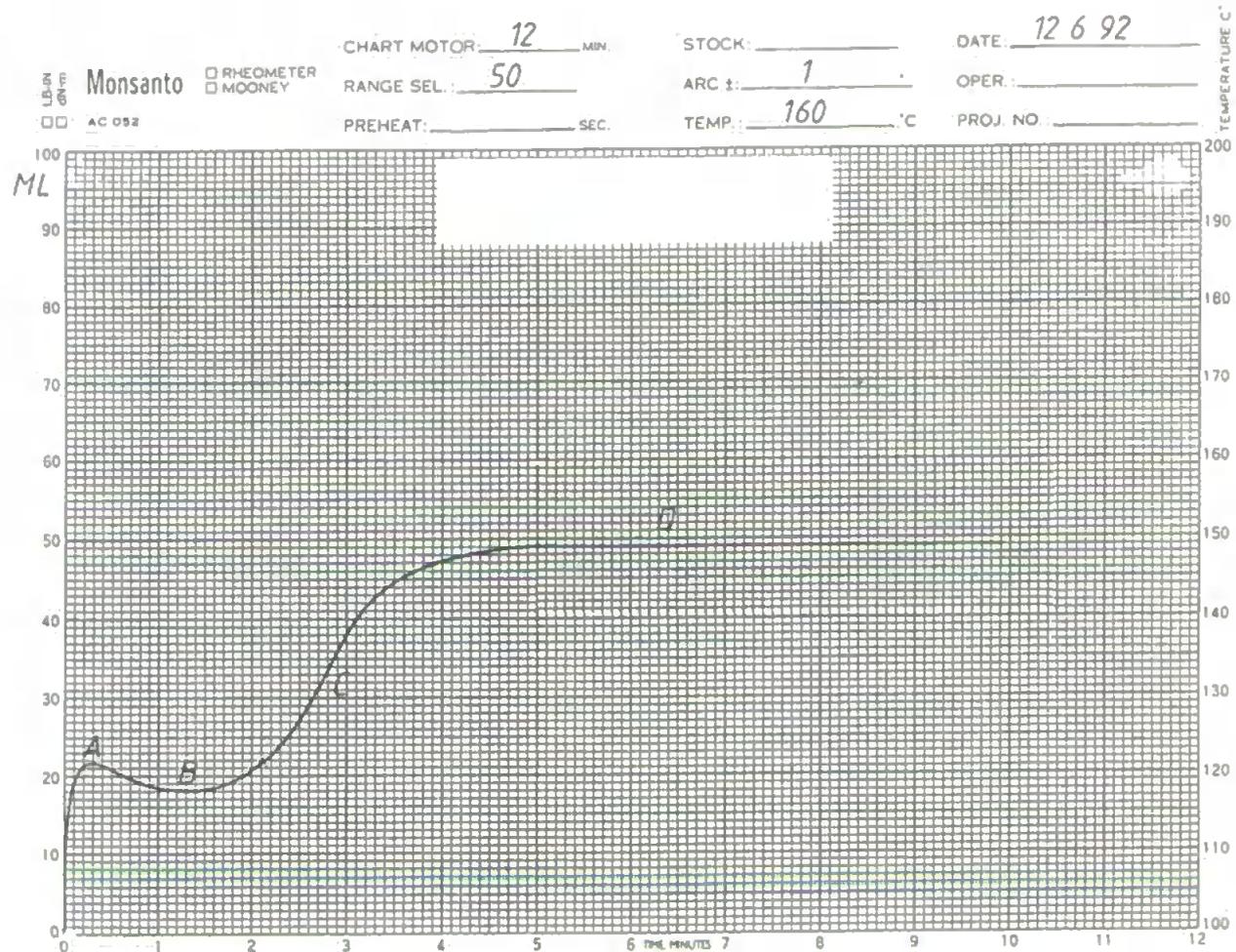
Membranes were hot pressed at a moulding temperature of 150°C as opposed to the rheological test temperature of 180°C because of the difference in rubber mass between the rheometer test piece (10g) and the membrane (0.5g) with a thickness of only 0.4mm.

5.4.2. Electrode Response

Discs 7mm in diameter were punched from the membrane and conditioned in either

Figure 5.3

Ideal Rheometer Curve



sodium chloride (10^{-1}M) sodium nitrate (10^{-1}M) or sodium perchlorate (10^{-1}M). The appropriately conditioned discs were assembled into electrodes and evaluated as chloride, nitrate and perchlorate ISEs respectively. All electrodes were non-responsive except for membrane H82 using purified bromobutyl rubber and 2.0% m/m of Diak No 1. This electrode gave a very small chloride response of $-17.3\text{mV decade}^{-1}$.

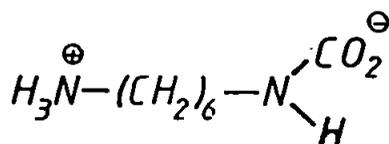
5.4.3 Nature of the Cross-link within the Bromobutyl Rubber Membranes

Although the membranes had proved to be unsuccessful, the nature of the cross-links was investigated. The two membranes with purified bromobutyl H81 and H82 were examined by infrared spectroscopy IR (infrared spectrometer IR 782, Perkin Elmer). The two membranes were extracted in a soxhlet extractor for 24 hours using methanol (BDH Spectrasol) as the solvent. The extracted membranes were then examined using transmission IR spectroscopy. Because the membranes had a relatively low tear strength it was not possible to vary film thickness by simply stretching the membrane. This resulted in excessive absorption for certain peaks especially those assignable to the polymer. Results were as follows for membrane H81, 1740 cm^{-1} (assignment $>\text{C}=\text{O}$). For membrane H82 the absorption bands were the same although with greater intensity at 1740cm^{-1} . Because of the previous extraction with methanol the results strongly supported the presence of a covalently bound $>\text{C}=\text{O}$ grouping. We could therefore conclude that the crosslinking agent Diak No. 1 shown in fig. 5.4 has been covalently bound within the polymer. The structure is most likely that suggested in

Section 5.4.1. However, because the quaternary ammonium group has no characteristic IR absorption band it is not possible to confirm its presence within the polymer.

Figure 5.4

Diak No 1



The electrode results for bromobutyl rubber membranes with the covalently bound quaternary groups would suggest that this is not an ideal polymer for the application. The poor compatibility between solvent mediators and the polymer may account for the disappointing electrochemical properties.

5.5 Neoprene and Carboxylated NBr Membranes

5.5.1 Composition and Fabrication

Neoprene rubber and carboxylated NBr contain unsaturation in the main polymer chain as shown in Section 2.2. Therefore it was possible to use the same immobilisation technique of unsaturated quaternary ammonium compounds and an organic peroxide. Membranes were fabricated by dissolution of the polymer in THF with addition of the DCP and triallylbutylammonium bromide (TABAB) with methanol. The composition of the membranes are shown in Table 5.11.

Table 5.11

Composition of Neoprene and Carboxylated NBr Matrix Membranes

Membrane Number	DCP/% m/m (pphr)	TABAB/% m/m (pphr)	Composition Notes Polymer
H85	12.1 (15.5)	9.3 (11.9)	Neoprene GRT
H86	12.1 (15.5)	9.3 (11.9)	Neoprene WRT
H87	12.1 (15.5)	9.3 (11.9)	Krynac 221

5.5.2 Electrode Response

Discs were punched from the membrane and conditioned for 7 days in potassium nitrate ($10^{-1}M$) solution. The electrode response was determined as described previously. Results are shown in Table 5.12

Table 5.12

Nitrate Electrode Response for Neoprene and Carboxylated Nitrile Rubber Membranes

Membrane Number	Slope/mV decade ⁻¹
H85	-21
H86	-23
H87	Non responsive

The use of solvent mediator free neoprene rubber membranes gave a small nitrate response not suitable for analytical purposes and therefore, limit of detection and $k_{NO_3^-, Cl^-}^{pot}$ were not evaluated. Carboxylated nitrile rubber gave non-responsive membranes. The results obtained in Section 4.4.2 with Krynac 19.65 showed that the addition of a suitable solvent mediator can produce Nernstian responses. Further work

with either neoprene or carboxylated nitrile rubber should focus on the use of plasticised membranes. A suitable solvent mediator would be 2-nitrophenyloctyl ether (2-NPOE).

5.6 'Hydrogenated' Nitrile Rubber Membranes

5.6.1 Tornac Rubber

A new polymer has recently been commercialised to perform at an elevated temperature and maintain oil resistance. Polysar have achieved this combination of properties by the introduction of the Tornac range of polymers [95]. During the polymerisation of poly (acrylonitrile-butadiene) the polymer is hydrogenated in solution. The reaction involves the use of a patented catalyst and hydrogen. The extent of hydrogenation can be controlled, for example, in the case of the polymer selected here, a level of 0.5 mol% unsaturation was used. The controlled unsaturation enabled the free radical initiated cross-linking and immobilisation technique to be used. With a lower level of unsaturation in the polymer it was expected that this would also favour radical formation within the QAS and so optimise immobilisation. The presence of unsaturation in the main polymer chain leads to so called ageing of the polymer. This occurs by either oxygen or ozone attack of the double bond and can proceed by auto oxidation leading to rapid loss of the physical properties. One possible mechanism for membrane failure was that of poor ageing properties of the polymer. The subject of membrane failure will be discussed further in Chapter 6. The use of a highly saturated poly(acrylonitrile-butadiene) polymer enabled the role of oxidative ageing and its influence on membrane lifetime to be assessed.

Results for the electrode response are shown below in Table 5.13:

Table 5.13

Lifetime Data for a Nitrate Electrode Using Membrane H77

Time/days	Slope/mV decade ⁻¹	Limit of detection/M
Original	-56.8	1 x 10 ⁻⁴
26	-54.3	8.9 x 10 ⁻⁵
67	-55.0	1.3 x 10 ⁻⁴
128	-57.1	7.9 x 10 ⁻⁵
222	-58.9	5.0 x 10 ⁻⁵
325	-55.4	7.9 x 10 ⁻⁵

The membrane gave a nitrate selective electrode with a long lifetime and $k_{NO_3^-, Cl^-}^{pot}$ value of 5×10^{-3} . These results are superior to a lifetime of only 4 months found for Krynac 50.75 membranes in Section 4.2.4 with the same composition as H77. The improvement in lifetime may be associated with improved oxidation resistance of the Tornac polymer.

5.7 Polymerisation of Triallylalkylammonium Bromides

Butler et al [99-107] successfully polymerised a range of quaternary ammonium salts (QASs) containing allyl groups. The most successful free radical initiator was tertiary-butylhydroperoxide (TBHP). Butler *et al* found that storage of the QAS and TBHP at 30°C for 10 days or 65°C for 24 hours produced water insoluble polymers from triallyl derivatives. These polymers were not formed in any specific configuration and

were not suitable for use as a membrane for an ISE.

In this work attempts to polymerise triallylbenzylammonium bromide with either TBHP or DCP were unsuccessful. The QAS and free radical initiator were dissolved in methanol to form a solution. The methanol was removed by evaporation and the residue placed on Melanex film. This was then hot pressed at 150°C for 10 minutes. The TABAB was found to melt and flow from the mould. Reduction of the temperature to 120°C and extension of the pressing time to 120 minutes did not achieve polymerisation.

5.8 Poly (Styrene-acrylonitrile) and Poly (Acrylonitrile-styrene-butadiene) Membranes

Earlier work in Chapter 4 suggested an improvement with changes to the ratio of butadiene and acrylonitrile. One option would have been to physically blend polybutadiene with nitrile rubber to provide membranes with a different acrylonitrile content. Problems of ensuring satisfactory blending prevented the use of polybutadiene. The polymers ABS and SAN are commercially available and unlike nitrile rubber are both plastics at room temperature. Because of this, both materials required the introduction of a solvent mediator to form rubbery or softer materials at room temperature. ABS contained unsaturation from the butadiene and therefore cross-linking and immobilisation using dicumyl peroxide was applicable. Membrane composition was as shown in Table 5.14.

Table 5.14**Composition of ABS and SAN Membranes**

Membrane Number	Polymer	TAOAB/%m/m (pphr)	DCP/%m/m (pphr)	2-NPOE/%m/m (pphr)
H78	ABS	6.5 (14.0)	7.2 (15.5)	39.7 (85.3)
H79	ABS	8.1 (14.0)	9.0 (15.5)	24.8 (42.6)
H80	ABS	7.2 (14.0)	10.3 (15.5)	14.1 (21.3)
H81	SAN	6.5 (14.0)	7.2 (15.5)	39.7 (85.3)
H82	SAN	9.0 (15.5)	9.0 (15.5)	24.8 (42.6)
H83	SAN	10.3 (15.5)	10.3 (15.5)	14.1 (21.3)

Membranes using 39.7 and 24.8% m/m of 2-NPOE were tacky, elastic, and lacked physical strength. This was such that both H78 and H81 could not be removed from the Melanex film. Both H79 and H82 formed discreet membranes but which distended when assembled into the electrode tip. Reduction of the solvent mediator to 14.1% m/m produced robust membranes which were rubbery in nature. When tested as nitrate selective electrodes after appropriate conditioning both membranes H79 and H82 gave sub-Nernstian responses with -18.4 and -10.4 mV decade⁻¹ respectively. The combination of the need for a solvent mediator and the poor physical strength of plastisiced membranes presented a major limitation for these two polymers. Neither appeared to be suitable as a matrix for the ion exchanger and did not offer advantages over nitrile rubber or the established PVC.

CHAPTER 6

Mechanistic Studies of the Covalently Bound QAS

Polymeric Membranes

6.1 The Conditioning Process

Commercially available poly(vinylchloride) (PVC) membrane ion selective electrodes (ISEs) require up to 24 hours for conditioning prior to use. The ion exchanger is already in the nitrate form and therefore it was assumed that only hydration of the membrane surface is necessary. With the SBS polymer matrix membranes with covalently bound quaternary ammonium salts (QAS) it was seen in section 3.1.2 that conditioning was complete within 1 day. The conditioning process must have included ion exchange (IX) of bromide for nitrate anions and presumably hydration of the membrane surface. In the present work it was found that poly(acrylonitrile-butadiene) (NBr) polymer matrix membranes in section 3.2.2 required up to 7 days to complete the conditioning process. This was of interest since the process of conditioning was expected to give an insight into the mechanism of response. The individual steps during the conditioning process were predicted to be:

- 1 hydration of membrane surface;
- 2 diffusion of NO_3^- into membrane;
- 3 ion exchange of NO_3^- for Br^- ;
- 4 diffusion of Br^- out of membrane.

Of these four steps the ion exchange process is known to be rapid and reversible since this is a prerequisite for a successful ion exchanger based ISE. Therefore the rate determining step must be dependent on diffusion or hydration steps. To test these

theories, a range of experiments were conducted as described below.

6.1.1 Monitoring the Conditioning Process of NBr Polymeric Membranes

A range of membranes were fabricated using triallylbenzylammonium bromide as the added ion exchanger. This was intended to assess the conditioning process for a covalently bound ion exchanger. In addition tripropylbenzylammonium bromide was also used, to include the effect of an entrapped ion exchanger within a cross-linked polymer matrix.

For both these QASs the nitrate form was used directly to prepare the membranes by conversion of the appropriate bromide salt. Either, TABzAB or TPBzAB (3.5g) was dissolved in distilled water (10ml) and silver nitrate solution (5g in 5ml) added dropwise, which resulted in a cream precipitation of silver bromide that rapidly darkened in daylight. The solution was filtered to enable further precipitation to be observed. A 2 drop excess of silver nitrate was added and the solution allowed to stand for 30 minutes. The excess silver nitrate was then precipitated by back titration with hydrochloric acid (0.005M). The solution was again filtered and water removed by rotary evaporation. The product was held under high vacuum to remove residual moisture and stored over anhydrous calcium chloride. After ion exchange treatment, triallylbenzylammonium nitrate (TABzAN) formed a waxy yellow solid and tripropylbenzylammonium nitrate (TPBzAN) formed a white solid.

The composition of the membranes are shown in Table 6.1 and all membranes were based on the 50% ACN content NBr polymer.

Table 6.1

Composition of Membranes to Investigate the Conditioning Process

Membrane Number	Ion Exchanger/% m/m (pphr)	DCP/% m/m (pphr)	Solvent Mediator/% m/m (pphr)
H84	TABzAB 10.2(13.1)	10.9 (14.0)	none
H85	TABzAN 9.7 (12.3)	11.1 (14.0)	none
H86	TPBzAB 10.4 (13.3)	11.0 (14.0)	none
H87	TPBzAN 9.9 (12.5)	11.0 (14.0)	none
H88	TABzAB 6.1 (13.0)	7.2 (15.5)	2-NPOE 39.9 (85.3)
H89	TABzAN 5.8 (12.3)	7.3 (15.5)	2-NPOE 40.0 (85.3)
H90	TPBzAB 6.1 (13.0)	7.2 (15.5)	2-NPOE 39.9 (85.3)
H91	TPBzAN 5.8 (12.3)	7.3 (15.5)	2-NPOE 40.0 (85.3)

6.1.2 Electrode Response During Conditioning

The membranes were conditioned as previously described in potassium nitrate solution ($10^{-1}M$). The electrode response was determined each day during the 7 day conditioning period. Results for the individual membranes are shown in Table 6.2 and the plot of response versus conditioning time is shown in figs. 6.1 and 6.2.

Table 6.2

Nitrate Electrode Response of Membranes During the Conditioning Process

Response	Membrane H84	Membrane H85	Membrane H86	Membrane H87	Membrane H88	Membrane H89	Membrane H90	Membrane H91
Day 1 Slope/mV decade ⁻¹	-8.9	-55.2	-3.7	-40.0	-43.4	-55.7	-13.7	-55.2
Day 2 Slope/mV decade ⁻¹	-9.6	-58.6	-11.4	-41.8	-48.7	-57.6	-31.9	-56.0
Day 3 Slope/mV decade ⁻¹	-15.1	-57.5	-18.8	-45.5	-56.0	-58.1	-26.6	-58.1
Day 4 Slope/mV decade ⁻¹	-25.1	-56.5	-35.6	-48.7	-56.5	-58.2	-49.7	-59.1
Day 5 Slope/mV decade ⁻¹	-38.2	-57.6	-40.9	-49.7	-56.0	-58.4	-50.8	-59.1
Day 6 Slope/mV decade ⁻¹	-45.5	-56.6	-44.5	-52.3	-55.9	-57.1	-51.3	-58.6
Day 7 Slope/mV decade ⁻¹	-45.6	-57.6	-41.9	-50.8	-56.0	-58.2	-52.8	-58.6
Added ion exchanger	TABzAB	TABzAN	TPBzAB	TPBzAN	TABzAB	TABzAN	TPBzAB	TPBzAN
Solvent Mediator	-	-	-	-	✓	✓	✓	✓

Figure 6.1

Electrode Response of Membranes without Solvent Mediator during the Conditioning Process

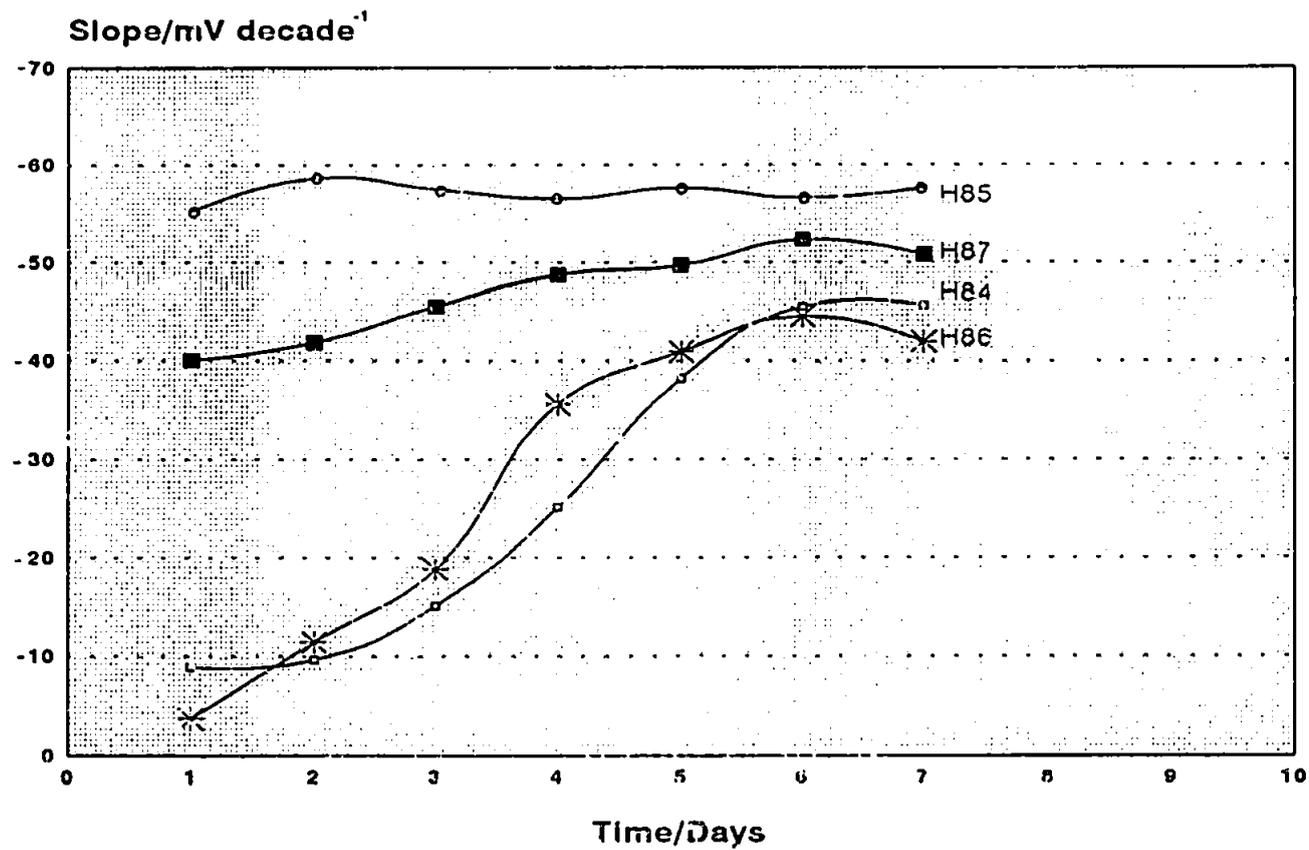
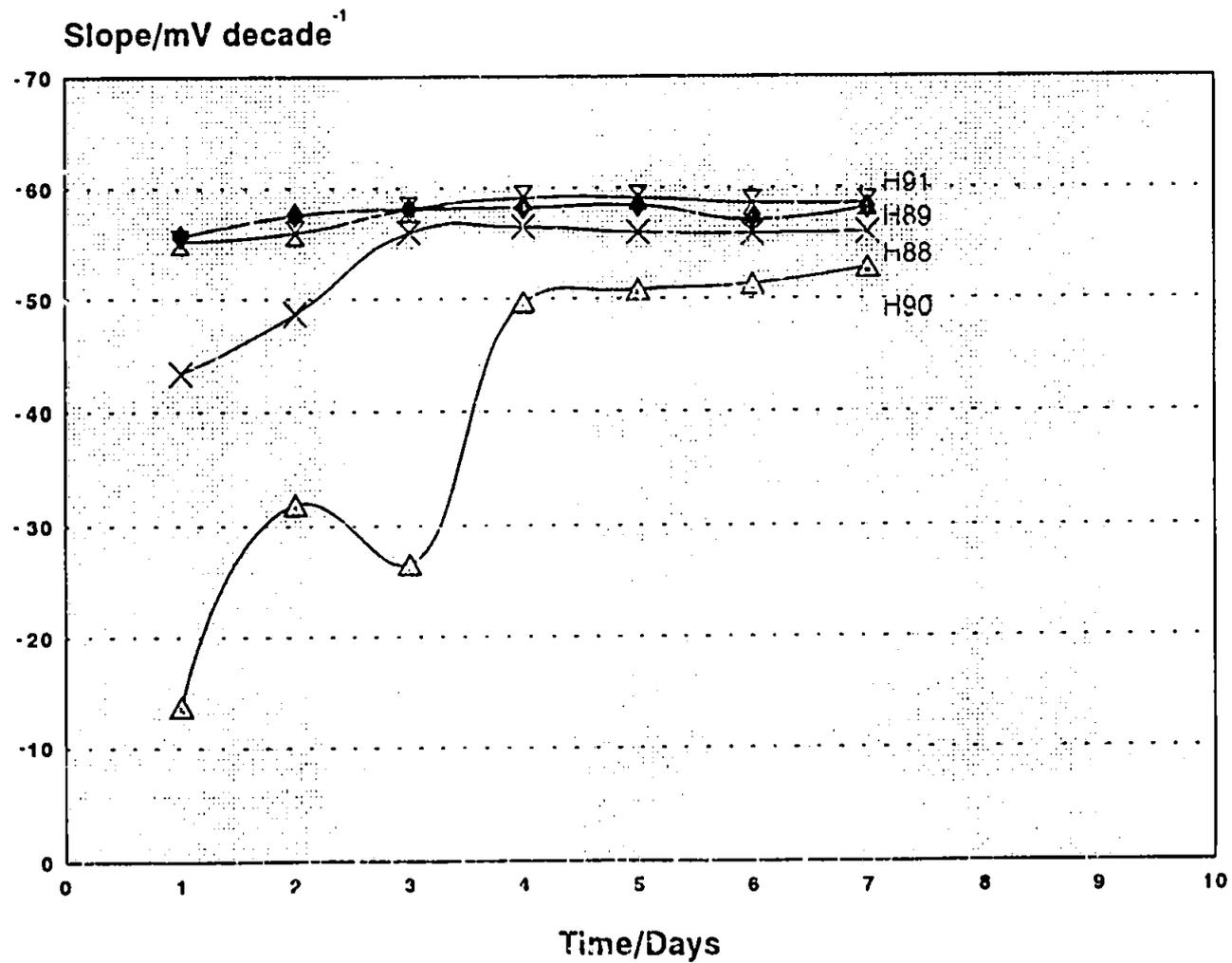


Figure 6.2

Electrode Response of Membranes with Solvent Mediator during the Conditioning Process



The data clearly showed the advantage of using an added ion exchanger which is already in the nitrate form because membranes H85 and H89 gave Nernstian responses after only 24 hours of conditioning. It was found that the presence of a solvent mediator speeded up the conditioning process achieving a Nernstian response after 3 days for H88 with TABzAB. The use of the same added ion exchanger in solvent mediator free membrane H84 required a full 6 days of conditioning to reach a response plateau. The introduction of solvent mediator is known to increase the permeability of the membrane and therefore a diffusion process was expected to be the rate limiting step.

The effect of hydration of the membrane surface was tested by immersion of membranes H84, H86, H88 and H90 in distilled water for 7 days. This was intended to hydrate the membrane surface. The membranes were then placed in the potassium nitrate ($10^{-1}M$) conditioning solution and the electrode response tested daily. The results are shown in Table 6.3 and the plot of response against conditioning time is shown in fig. 6.3.

Interestingly the hydration of the membrane surface prior to conditioning did not affect the response characteristics for the membranes over the 7 day period. This is in agreement with the previous results for the nitrate form of the ion exchanger which gave Nernstian responses after 24 hours. It was concluded that the rate determining step was associated with the diffusion of either nitrate into the membrane or bromide anions into the conditioning solution.

Figure 6.3

Electrode Response for Hydrated Membranes during the Conditioning Process

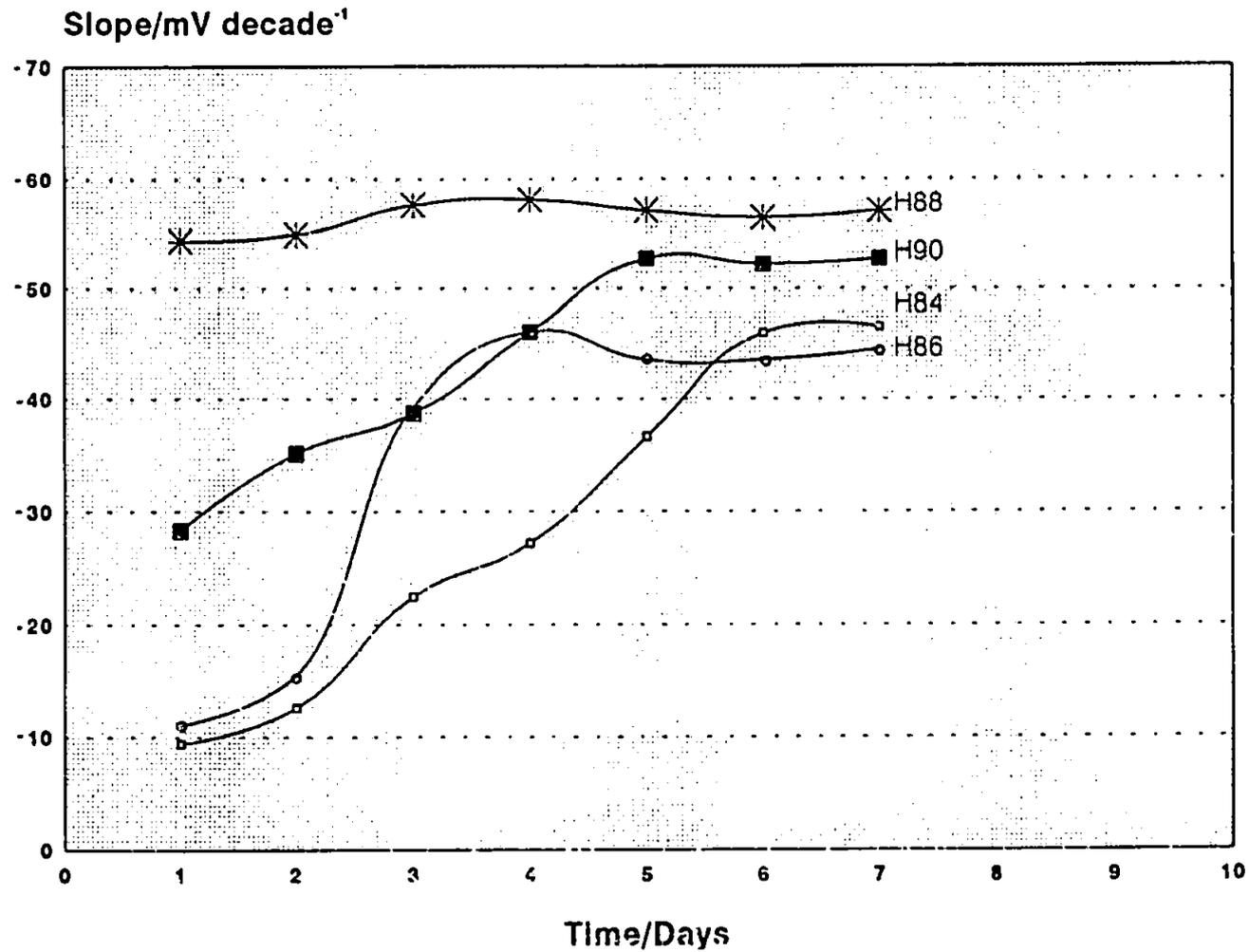


Table 6.3

Nitrate Electrode Response for Hydrated Membranes

Electrode Response	Membrane H84	Membrane H86	Membrane H88	Membrane H90
Day 1 Slope/mV decade ⁻¹	-9.4	-11.0	-54.4	-28.3
Day 2 Slope/mV decade ⁻¹	-12.6	-15.2	-55.0	-35.1
Day 3 Slope/mV decade ⁻¹	-22.5	-39.3	-57.6	-38.7
Day 4 Slope/mV decade ⁻¹	-27.2	-46.1	-58.1	-46.1
Day 5 Slope/mV decade ⁻¹	-36.6	-43.5	-57.1	-52.8
Day 6 Slope/mV decade ⁻¹	-46.0	-43.5	-56.5	-52.3
Day 7 Slope/mV decade ⁻¹	-46.6	-43.5	-57.1	-52.8
Added Ion Exchanger	TABzAB	TPBzAB	TABzAB	TPBzAB
Solvent Mediator	-	-	✓	✓

6.1.3 Ion Exchange of Nitrate for Bromide Anions

The process of ion exchange between bromide and nitrate is limited by the diffusion of the ions through the polymer matrix. Ideally the diffusion of nitrate anions within the membrane bulk should be monitored but this was not possible with the available surface microscopy techniques. The process of ion exchange was, however, monitored by quantifying the release of bromide anions into the potassium nitrate conditioning solution over a 32 day period as described in section 2.10. The ion exchange process was monitored in duplicate using punched membrane discs with a 27.9mm diameter and total surface area of 12.5 cm². Membranes H84 and H88 were tested and the results are shown in Table 6.4 and a plot of bromide concentration against conditioning time is shown in fig. 6.4.

Table 6.4

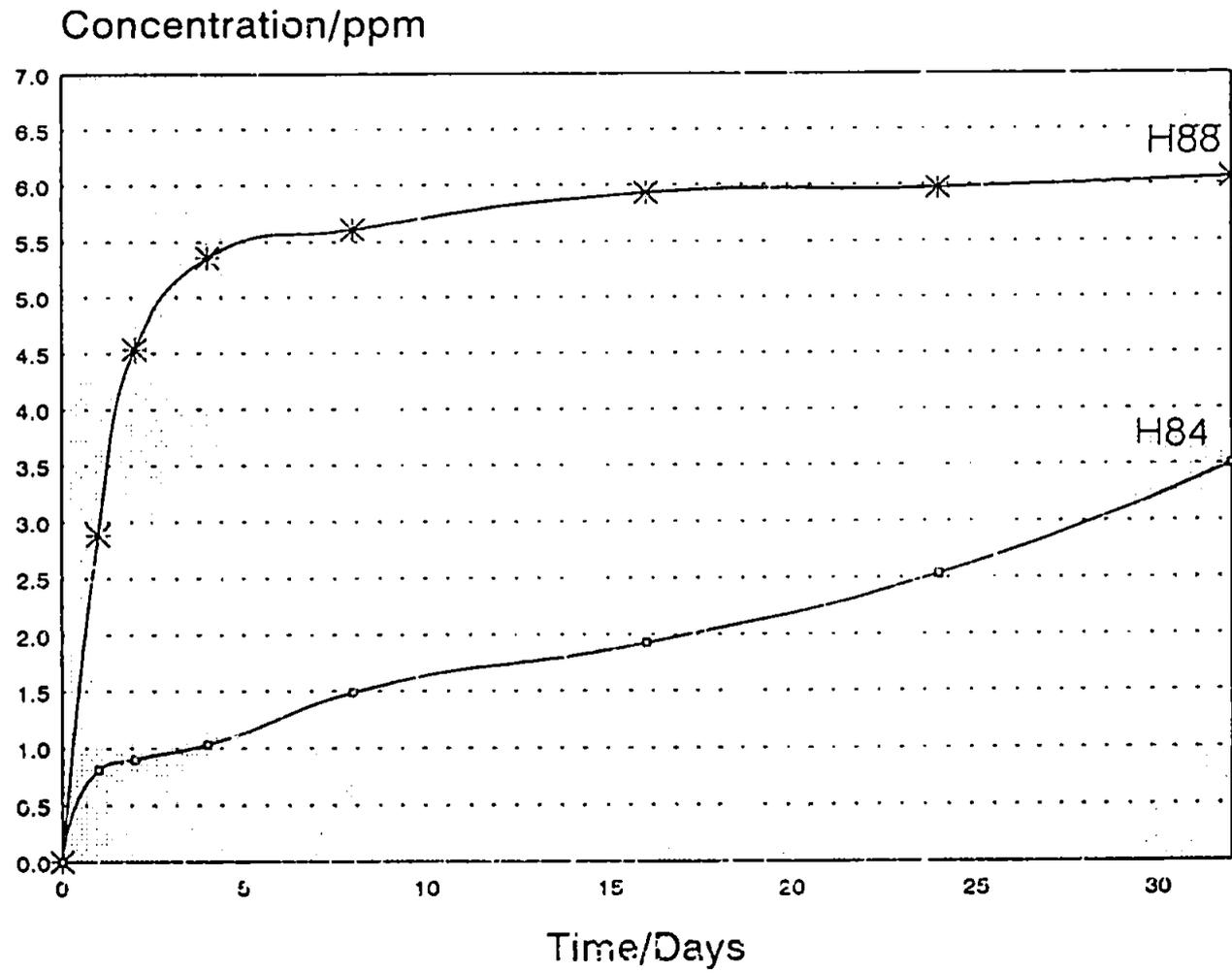
Conditioning Solution Bromide Concentration in Parts per Million (ppm) Following Ion Exchange

Time/Days	Bromide Conc./ppm			
	Membrane H84		Membrane H88	
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
1	0.85	0.7	3.3	2.47
2	0.84	0.95	4.04	5.03
4	1.03	1.03	5.11	6.60
8	1.63	1.35	5.36	5.86
16	2.05	1.81	5.88	5.97
24	2.57	2.48	5.98	5.95
32	3.42	3.58	6.03	6.10

These results illustrate a significant difference between the two membranes and demonstrate the effect of the solvent mediator in membrane H88. There was a higher level of TABzAB (10.2% m/m) in H84 compared to H88 (6.1% m/m) and yet a greater level of ion exchange occurred with the latter membrane. After 8 days the ion exchange process reached a plateau for H88 and calculations confirmed that further bromide anions were still held within the membrane. There are two possible explanations for the observed behaviour. Either the presence of a solvent mediator has increased the diffusion rate and accelerated the conditioning process or alternatively the selectivity of the membrane has been affected.

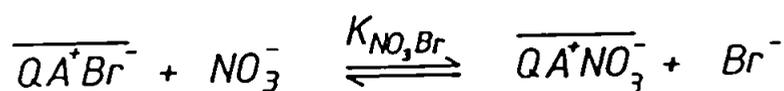
Figure 6.4

Conditioning Solution Bromide Concentration (ppm) Following Ion Exchange



Complete ion exchange (IX) of bromide for nitrate would have given a solution bromide concentration as follows, membrane H84 a. 16.2 ppm b. 18.7 ppm and membrane H88 a. 8.2 ppm and b. 8.5 ppm. The concentration of the conditioning potassium nitrate solution was $10^{-1}M$ whilst the averaged concentration of released or ion exchanged bromide for membrane H88 was $7.6 \times 10^{-5}M$ after 32 days. Maximum ion exchange of bromide for nitrate in membrane H88 would have produced an averaged bromide concentration of $1.04 \times 10^{-4}M$. The equilibrium constant (selectivity coefficient) of the exchange reaction can be shown as follows [116].

Anion Exchange



The $\overline{\quad}$ denotes the stationary phase and $k_{NO_3,Br}$ the selectivity coefficient for the ion exchange process given by the following equation

$$K_{NO_3,Br} = \frac{[\overline{QA^+NO_3^-}][Br^-]}{[\overline{QA^+Br^-}][NO_3^-]}$$

To calculate both $[QA^+ NO_3^-]$ and $[QA^+ Br^-]$ the volume of the membrane was required. The averaged dimensions of the test membrane H88 a and b were, diameter 27.9 mm, thickness 0.4mm and total volume of 244.5mm³. The average mass of H88 a and b was 0.1592g and there was 5.32×10^{-5} mol TABzAB in 2.445×10^{-4} dm³ of membrane. Therefore, $[QA^+ Br^-]$ was equal to 0.218 mol dm⁻³. The proportion of $QA^+ Br^-$ that was exchanged to $QA^+ NO_3^-$ is given by the relationship between the exchanged bromide and total available bromide, 6.06/8.35. Therefore $[QA^+ NO_3^-]$ was equal to 0.158 mol dm⁻³. Substitution into the equilibrium equation gives:

$$K_{NO_3, Br} = \frac{[QA^+ NO_3^-][Br^-]}{[QA^+ Br^-][NO_3^-]}$$

Under the conditions tested, membrane H88 has a selectivity for nitrate over bromide anions of 5.5×10^{-4} . This compares to a $k_{NO_3^-, Br^-}^{pot}$ value of 5×10^{-2} determined with a constant interferent of potassium bromide ($10^{-2}M$). The plateau for bromide release in membrane H88 therefore appears to be a function of the membrane selectivity.

6.2 Method of Membrane Failure

We have described membrane failure as being a fall in response such that a sub-Nernstian slope was produced. This is widely regarded as a slope of less than -55 mV decade⁻¹, [22] although in many cases we continued taking measurements down to

slopes of -40mV decade^{-1} . Lifetime data for triallyloctylammonium bromide containing membranes from section 5.1.3 was plotted to produce figs. 6.5 and 6.6. Electrode failure occurred suddenly for the cross-linked membranes, however for membrane H62 using an entrapped ion exchanger, the response fell constantly. This was believed to be due to the slow diffusion of ion exchanger from the membrane into solution. This behaviour marked a stark difference in failure characteristics between that of entrapped and immobilised ion exchanger. A number of possibilities for loss of membrane responsiveness for immobilised ion exchanger membranes were considered as shown below:

- 1 extensive hydration of the membrane;
- 2 extraction of mediator;
- 3 extraction of electroactive moieties within the polymer;
- 4 chemical degradation of ion exchanger groups possibly by oxidation;
- 5 catastrophic physical failure of the membrane.

6.2.1 Extensive Membrane Hydration

As a means of investigating the mechanism of membrane failure, attempts were made in effect, to revitalise failed membranes. To evaluate the role of extensive hydration, a number of membranes from section 4.2.2 were taken after 6 months storage in a conditioning solution and dried for 7 days over anhydrous calcium chloride. These membranes were then tested immediately for response to potassium nitrate standards and tested again after 1 and 7 days conditioning. Test results and composition data are shown in Table 6.5.

Figure 6.5

Lifetime Plots for 50% ACN NBr Membranes with TAOAB as the Ion Exchanger

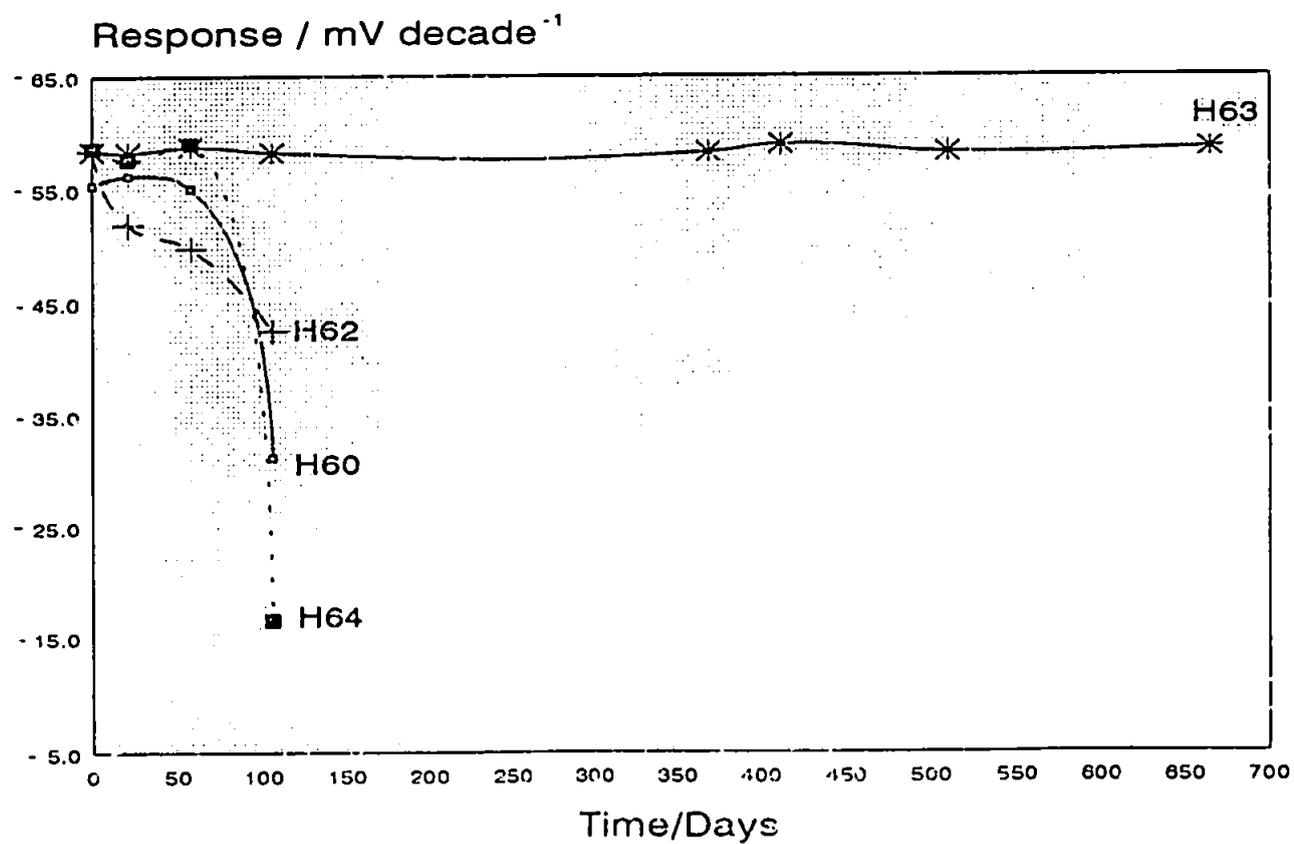


Figure 6.6

Lifetime Plots for Varying ACN NBr Membranes with TAOAB as the Ion Exchanger

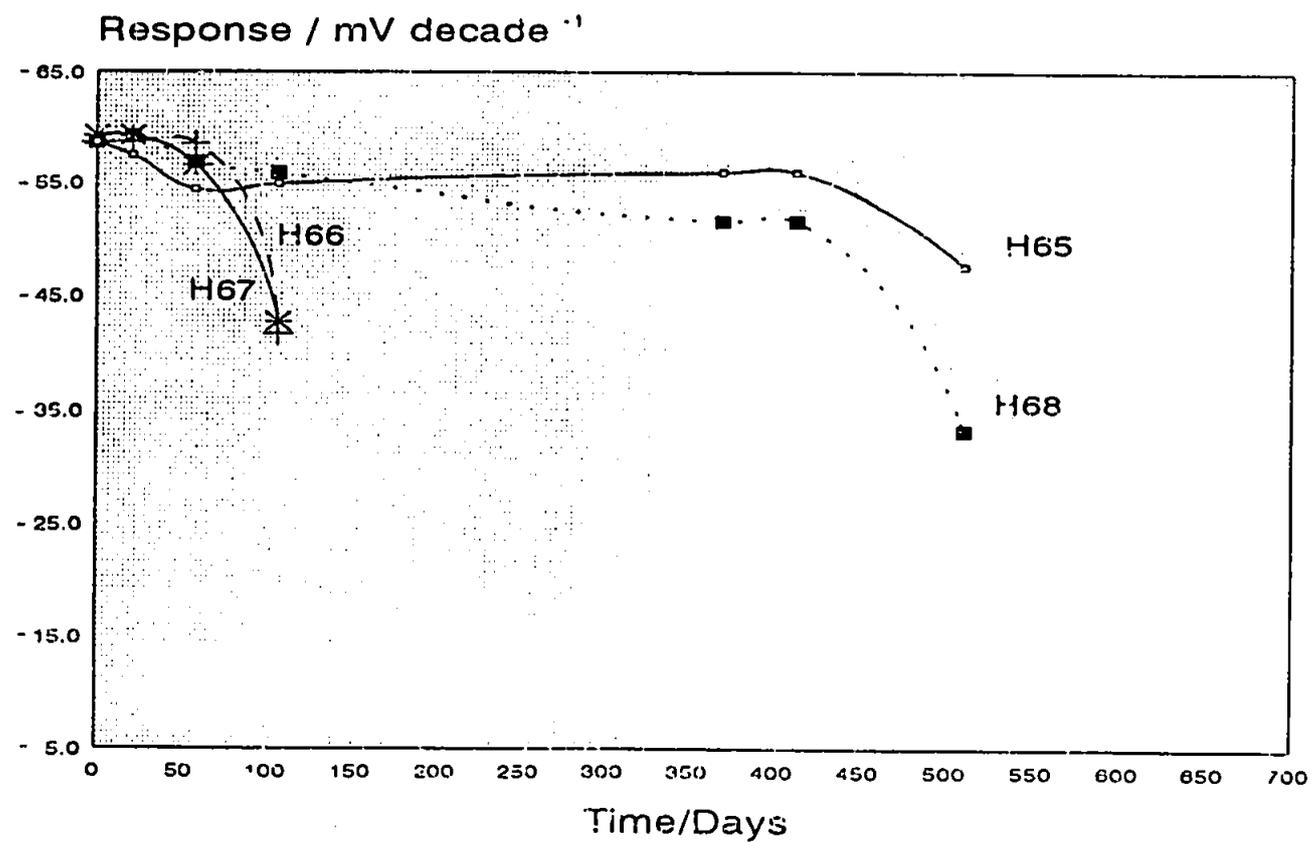


Table 6.5

Nitrate Electrode Response for Revitalised Membranes

Membrane Number	Original Slope/mV decade ⁻¹	After Storage Slope/mV decade ⁻¹	Dried Slope/mV decade ⁻¹	Reconditioned Slope/mV decade ⁻¹	7 Days Storage Slope/mV decade ⁻¹
H13	-55.5	-20.0	-31.5	-30.2	-21.3
H17	-58.9	-48.1	-37.5	-53.4	-52.8
H18	-58.1	-31.7	-11.3	-43.3	-23.7
H21	-57.9	-31.6	-29.4	-41.2	-30.1

These results show that a degree of membrane hydration is necessary to give an electrode response. After 1 day reconditioning the membranes all gave very similar responses to that experienced before membrane drying. In certain cases the slope was better but, after 7 days conditioning, this slight (-10mV decade⁻¹) improvement was lost. Membrane hydration although necessary to give functioning electrodes is not a primary cause of the reduction or fall off in response noted with membranes H13, H17, H18 and H21.

6.2.2 Reduced Ion Exchanger Levels

To assess the role of reduced ion exchanger levels, a range of membranes were fabricated with varying levels of triallyloctylammonium bromide. The level of ion exchanger was progressively reduced by 50% on a m/m basis. Membrane compositions are shown below and the 50% ACN content NBr polymer was used.

Table 6.6

Composition of Membranes Fabricated with Reduced Ion Exchanger

Membrane Number	TAOAB/%m/m (pphr)	DCP/%m/m (pphr)	Solvent Mediator %m/m (pphr)
H92	4.0 (4.65)	9.0 (10.3)	none
H93	2.0 (2.3)	9.2 (10.3)	none
H94	0.8 (0.9)	9.3 (10.3)	none
H95	3.3 (7.0)	7.4 (15.5)	2-NPOE 41.1 (85.3)
H96	1.7 (3.4)	7.5 (15.5)	2-NPOE 41.8 (85.3)
H97	0.7 (1.3)	7.7 (15.5)	2-NPOE 42.2 (85.3)

The electrode response was determined as described earlier and the results are shown in Table 6.7.

Table 6.7

Nitrate Electrode Response With Reduced Ion Exchanger Levels

Membrane Number	Slope/mV decade ⁻¹	Limit of Detection/M	$k_{NO_3^-, Cl^-}^{pot}$
H92	-26.3	-	-
H93	-26.9	-	-
H94	-30.9	-	-
H95	-57.1	4.2×10^{-5}	8.9×10^{-3}
H96	-48.8	1.5×10^{-4}	2×10^{-2}
H97	-50.4	8.3×10^{-5}	2×10^{-2}

From this data it was not possible to identify a direct relationship between electrode response and level of ion exchanger within the membrane matrix. The presence of a

solvent mediator in membranes H95 to H97, appeared, to facilitate the electrode response even with reduced ion exchanger. For the membranes H92 - H94 fabricated without a solvent mediator and reduced ion exchanger, the electrode response was significantly affected. We can conclude that the solvent mediator plays an important role in the process and has enhanced the response of the ion exchanger. The loss of response of the membrane could be due to chemical degradation of the immobilised ion exchanger by auto-oxidative attack of the unsaturated allyl groups. It is possible that as the immobilised ion exchanger is degraded by oxidation, the presence of the 2-NPOE may enable the reduced level of active ion exchanger to maintain an electrode response. The behaviour noted offers one possible explanation for the extended lifetime exhibited by 2-NPOE solvent mediator containing membranes. Alternatively, the solvent mediator may impart some degree of antioxidant properties to the membrane, however, such properties have not been associated with 2-NPOE.

6.3 Extent of Quaternary Ammonium Salt Immobilisation

In previous studies [85] the extent of QAS immobilisation was determined by solvent extraction of the membrane and subsequent Kjeldahl analysis. This allowed determination of the level of nitrogen in the membrane and was based on the fact that non-immobilised QAS had been removed by the solvent extraction. The polymer used was poly(styrene-b-butadiene-styrene) (SBS) which did not contain nitrogen. In this work such an approach was not possible because the chosen polymer NBr contained nitrogen from the acrylonitrile. The work by King [85] showed that between 54% and 71% of quaternary ammonium nitrogen was covalently bound to the polymer. This was lower than expected and attempts such as increased QAS loading did not improve the % bound figure. Increasing the ratio of initiator to QAS did result in a higher

degree of quaternary ammonium immobilisation.

Alternative methods of quantifying immobilised QAS were considered based upon membrane extraction and analysis of the extract. The quaternary ammonium salts lacked suitable structural features for detection either within the membrane or alternatively after extraction in a solvent. There were no useful infrared absorption bands that could be utilised for detection because the poly(acrylonitrile-butadiene) would duplicate the response from the alkyl and allyl groups. The ultra violet spectrum (UV) for the triallylammonium derivatives had an absorption maximum below 200nm which was considered unsuitable for analytical purposes. In this work the aim was to detect and confirm the presence of the quaternary ammonium group rather than the counter ion. To enable detection of the QA^+ groups, a model ion exchanger triallylbenzylammonium bromide (TABzAB) was synthesised which incorporated a functional group enabling detection by UV spectroscopy with an absorption maximum at 260-270nm.

The use of labelled compounds either ^{14}C , ^{13}C or ^{15}N could have enabled techniques such as scintillation counting or nuclear magnetic resonance (NMR) to have been used. The use of either ^{13}C or ^{15}N NMR would have ideally required the analysis of the solid membrane and consequently involved extensive method development. The bromide counter ion can be detected using X-ray emission analysis. This method was used in a semi-quantitative way with a scanning electron microscope fitted with an energy dispersive X-ray analyser (EXDA). These data are included in section 6.5.2 but yield information only on the counter ion.

6.3.1 Membrane Extraction and Ultra Violet Spectrometric Detection

The most important factor when extraction of a polymeric material is undertaken is the selection of a suitable solvent. An ideal solvent should swell the polymer, have a low boiling point, dissolve potential extractives but not react with them. Methanol fulfilled these requirements and was recommended in the literature [117].

The stability of triallylbenzylammonium bromide in methanol was confirmed by refluxing a dilute solution for 7 days and measuring the absorption maximum at 262.4nm over that period. A calibration curve was constructed and the molar absorptivity E was calculated as $363.9 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The molar absorptivity E was determined for tripropylbenzylammonium bromide and found to be $380.2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The calibration was found to obey Beers Law up to an absorbance of one where:

$$\log \frac{I_0}{I} = Ecl$$

and

$$\log \frac{I_0}{I} = \text{absorbance}$$

E = molar absorptivity $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$;

c = concentration mol dm^{-3} ;

l = path length cm .

The detection limit for the UV spectrometric method was determined by repeated absorbance measurement at 262.4nm of a $1.28 \times 10^{-4} \text{M}$ TABzAB solution. A blank was determined between readings and the detection limit was calculated using the formula:

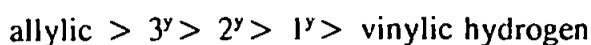
$$\frac{2 \times SD \times \text{conc.}_{\text{std}}}{\text{mean}} = \text{limit of detection}$$

where SD = the standard deviation of the repeated absorbance measurement.

The limit of detection was $2.7 \times 10^{-5} \text{M}$.

Extraction of the membrane was completed using a 250ml soxhlet apparatus and 200ml of methanol (Spectrosol BDH). It is common practice to dice or cut the materials into small cubes of about 3mm per side. Because the membranes were of the order of 0.4mm thick it was concluded that this step was unnecessary. The membrane was extracted by reflux for 7 days to ensure complete extraction.

The UV detection of TABzAB in the methanol extract solution necessitated the replacement of other aromatic components in the membrane composition. The aromatic initiator dicumyl peroxide was replaced by the aliphatic tert-butylhydroperoxide to overcome interference from DCP. Previously in section 4.2 the use of DCP had been shown to give an improved cross-link density compared to the use of TBHP. It was only possible to extract those membranes which did not include a solvent mediator since both dibutyl phthalate (DBP) and 2-NPOE would have interfered with the detection of TABzAB. Membranes were also fabricated using tripropylbenzylammonium bromide TPBzAB as the ion exchanger. The replacement of the unsaturated allyl groups by the saturated propyl group was predicted to affect the immobilisation reaction. The abstraction of hydrogen becomes progressively more difficult in the following series [118]:



Because it is more difficult to extract hydrogen from the propyl group then abstraction of hydrogen from the unsaturated sites of the polymer will be favoured. Membranes were fabricated using the 50% ACN polymer and are shown in Table 6.8.

Table 6.8

Composition of Methanol Extracted Membranes

Membrane Number	TBHP/%m/m (pphr)	TABzAB/%m/m (pphr)	TPBzAB/%m/m (pphr)
H92	9.5 (11.6)	9.9 (12.2)	-
H93	9.4 (11.6)	-	10.1 (12.5)
H94	-	10.9 (12.2)	-
H95	-	-	11.1 (12.5)
H96	8.6 (11.6)	17.7 (2.4)	-
H97	10.4 (11.6)	-	-

Each membrane was fabricated and extracted in duplicate. The methanol extract was made up to volume and the absorbance determined at 262.4 nm to enable the amount of extracted TABzAB or TPBzAB to be quantified. The mass of QAS available for extraction was calculated to enable % of QAS immobilised in the membrane to be established.

Table 6.9

Ultra Violet Spectrometric Results for Methanol Extracts

Membrane Number	A at 262.4nm	Mass of Membrane/g	Mass of extracted QAS/g	Mass of extracted QAS/mg	QAS extracted/%	Immobilised QAS/%
H92 a	0.037	0.812	0.080	4.8	6.0	94.0
H92 b	0.030	0.685	0.067	3.8	5.7	94.3
H93 a	0.098	0.817	0.082	13.3	16.2	83.8
H93 b	0.105	0.817	0.082	14.2	17.3	82.7
H94 a	0.015	0.758	0.082	3.0	3.6	96.4
H94 b	0.015	0.763	0.083	3.0	3.6	96.4
H95 a	0.158	0.794	0.088	20.9	23.7	76.3
H95 b	0.158	0.837	0.092	20.9	22.5	77.4
H96 a	0.127	0.795	0.141	16.6	11.8	88.1
H96 b	0.120	0.791	0.140	15.9	11.4	88.6

The % QAS immobilisation for membranes H92 and H96 are very encouraging showing a 94 and 88% covalent attachment. The increase in TABzAB in H96 with a constant pphr of TBHP resulted in an increased level of QAS immobilisation but reduced % attachment. Membranes H93, H94 and H95 were intended to act as a means of determining % recovery. It was expected that H94 and H95 which did not contain an initiator would give 100% recovery of the QAS. The use of TABzAB in membrane H94 gave 96% QAS immobilisation whilst the tripropyl derivative gave 77% attachment. This is somewhat lower than that obtained in membrane H93 using TPBzAB and an initiator where 83% immobilisation resulted. These results cast considerable doubt on the analytical method and indeed the encouraging results for membranes H93 and H96. Immobilisation requires a free radical initiator to proceed although there is evidence to support covalent attachment of the propyl derivative. Abstraction of a tertiary hydrogen is far more difficult than an allylic hydrogen. It is however possible and this is confirmed by evidence of free radical initiated cross-linking of saturated ethylene propylene copolymers [93]. There is no evidence to support self initiation as would be required to explain the high % immobilisation recorded for membranes H94 and H95.

The use of methanol as an extractive solvent is well supported by the literature and is considered to be a suitable solvent. The detection method of UV spectroscopy had been optimised by the incorporation of the UV active benzyl group in the QAS. There was however an unexpected problem associated with the polymer matrix poly(acrylonitrile-butadiene) with a large background absorption evident at 230nm and an absorbance of around 1 at 260nm. The detection of a small absorption band against

such a large background was regarded as a potential source of error.

To overcome this problem, it was decided to purify the polymer prior to use in extraction studies. Previously the NBr polymer had been purified by dissolution in tetrahydrofuran (THF) and precipitated using methanol. As received NBr polymer (Krynac 50.75) (10g) was placed in a soxhlet extraction apparatus and extracted with methanol (Spectrosol)(150ml). After 7 days fresh methanol was used and the extraction continued for a further 4 days. Absorption values are shown in Table 6.10 and indicate the level of extractions from the polymer.

A portion of fresh methanol was used after 11 days and the extraction continued for a further week. At this stage the UV absorption at 262.4nm had an absorbance of 0.081 and it was concluded that the polymer was sufficiently clean for use in the fabrication of membranes. One concerning feature was the high level of extractions after a long period of time. These results suggested that the polymer may be decomposing with time and releasing additional solvent soluble material.

A 50ml portion of the extract solution was taken and the methanol was removed by rotary evaporation. The resultant residue was mixed with potassium bromide (0.1g) (BDH Spectrosol) and ground in a pestal and mortar to form a KBr disc. The infrared (IR) spectrum was recorded using an IR spectrophotometer (IR 782, Perkin Elmer Ltd., Beaconsfield, Bucks UK). The major peaks observed were 2240cm^{-1} -C \equiv N stretch present (assignment aliphatic nitrile group), 1070cm^{-1} 960cm^{-1} 720cm^{-1} =CH₂ rock (assignment methyl group). Based on the possible assignments it was concluded that

the polymer was slowly degrading and thereby releasing further solvent extractable residues. This conclusion would suggest that a certain background level of extractable material was inevitable with the chosen NBr polymer.

Table 6.10

Absorption Values for Methanol Extracts of NBr Polymers

Time/Days	Absorbance at 230nm	Fresh Methanol Absorbance at 262.4nm
0	0	-
1	3.64	-
2	3.8	-
3	3.8	-
4	3.8	-
5	3.9	-
6	3.8	-
7	3.8	-
8	-	0.020
9	-	0.053
10	-	0.171
11	-	3.54

To assess the effect of the pre-extracted polymer, the membranes listed in Table 6.7 were refabricated with the polymer purified as described above. The membrane composition is shown in Table 6.11.

Table 6.11

"Purified" NBR polymer membranes for Methanol Extraction.

Membrane Number	TBHP/%m/m (pphr)	TABzAB/%m/m (pphr)	TPBzAB/%m/m (pphr)
H98	9.5 (11.6)	9.9 (12.2)	-
H99	9.4 (11.6)	-	10.1 (12.5)
H100	-	10.9 (12.2)	-
H101	-	-	11.1 (12.5)
H102	8.6 (11.6)	17.7 (2.4)	-
H103	10.4 (11.6)	-	-

The membranes were fabricated in duplicate and solvent extracted with methanol as previously described. The UV Spectra were recorded and there was a background absorbance of 0.6 which was again considered to be too high to enable reliable determinations for the extracted QAS.

6.3.2 Ion Exchange Chromatography

The methanol extracts described in section 6.3.1. were prepared with the intention of quantification of the quaternary ammonium salt (QAS) using UV spectroscopy. Because of the difficulties described above, ion exchange (IX) chromatography was considered. It is possible to successfully determine bromide concentration using ion exchange chromatography (IX) as illustrated in section 6.1.3. For each QA⁺ group extracted

with methanol there must be a corresponding counter ion. The assumption that each bromide anion in solution would represent a QA^+ ion was considered invalid because moisture within the membrane or methanol could give rise to ion exchange.

6.3.3 Cation Exchange

An alternative to anion determination was direct quantification of the QA^+ ion using a cation exchange column. The same equipment as described in section 2.10 was used with a cation column (IC Pak-C) (Waters Chromatography) Milford, Massachusetts, USA) and guard column (IC Pak-C-guard column) (Waters Chromatography). The eluent used was a 0.05mM EDTA/2mM HNO_3 solution at a flow rate of 1.2ml/min. Standards of both triallylbenzylammonium bromide and tripropylbenzylammonium bromide were prepared by serial dilution in distilled water (AnalaR BDH) in the range 1 to 16 ppm of TABzAB or TPBzAB. A problem of QA^+ retention was noted which did not occur when a standard containing Li^+ K^+ Na^+ and NH_4^+ was run. One explanation for retention on the column was that of reverse phase interaction [116]. The mobile phase was therefore modified by the introduction of 10% acetonitrile, but this did not resolve the problem of column retention and analysis was not possible. Further addition of acetonitrile was not recommended because this would have resulted in the removal of the stationary phase.

Successful separation of the QA^+ group would require an alternative column. The IC-Pak-C-MD [119] was specifically recommended for the determination of quaternary ammonium compounds and is able to tolerate a mobile phase with up to 30% acetonitrile. A combination of column availability and time prevented further analytical work.

6.4 Optical Microscopy

The electrode lifetime measurements in section 5.1.3. using membranes fabricated with triallyloctylammonium bromide (TAOAB) showed a large dependency on composition.

Membrane H60 fabricated using the 50% ACN content NBr polymer, dicumyl peroxide and TAOAB maintained a Nernstian response to nitrate for less than 100 days. The addition of the solvent mediator 2-nitrophenyloctyl ether (2-NPOE) in membrane H63 resulted in a Nernstian response to nitrate for in excess of 665 days.

The surface of the individual membranes H60 and H63 were examined by optical microscopy and recorded by photography. An optical microscope Olympus BH2 (Olympus UK, London, England) was used fitted with a camera and automatic exposure unit (C-35 AD-2 OECU, Olympus). The exposure time ranged from 0.5 to 30 seconds and was dependent on the level of background lighting and membrane transparency. A Kodacolor Gold ASA 100 film (Kodak, USA) was used to provide a permanent record of the observed membrane surface.

The expectation was that evidence may be obtained to explain the difference in behaviour. Membranes were also examined both before and after being conditioned for 100 days in 10^{-1}M KNO_3 solution. In certain cases [85], membrane failure had been attributed to the lack of physical strength. This type of defect would have been apparent using microscopical examination as small flaws or cracks on the membrane surface. The surface of H62 was also examined which contained just polymer and cross-linking agent.

6.4.1 Results of Visual Microscopy Examination

Photographs obtained using the optical microscope are shown in plates 6.1 to 6.6. At x200 magnification it was possible to observe a large number of particles both on the surface and in the bulk of the membrane. Examination of the membranes both before and after conditioning confirmed the freedom from surface flaws or cracks. There was no evidence of physical degradation of the membrane after the conditioning process and therefore this was eliminated as a potential explanation for electrode failure.

Imperfections such as air bubbles were enlarged during the conditioning process by water due to the osmotic effect. This was caused by the high QAS concentration within the membrane. The hydration of the surface during conditioning resulted in the membrane becoming opaque. The particles on the conditioned membrane surface were not expected to be KNO_3 because the surface was rinsed with distilled water prior to examination. The materials were obviously not soluble in water and the exact composition was considered intriguing. Information as to the source or identification of the particle size was not available from visual microscopical examination. For this reason alternative techniques were considered to enable characterisation of the particles.

Plate 6.1

H60 x 200 Magnification Original

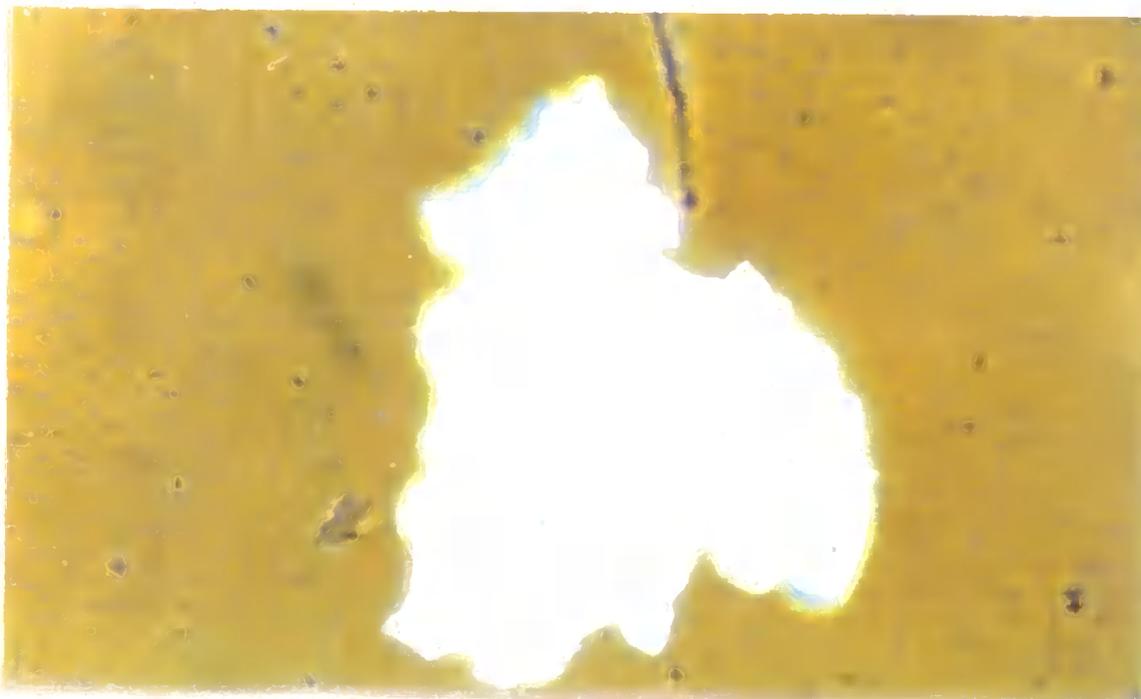


Plate 6.2

H60 x 200 Magnification Conditioned



Plate 6.3

H63 x 200 Magnification Original

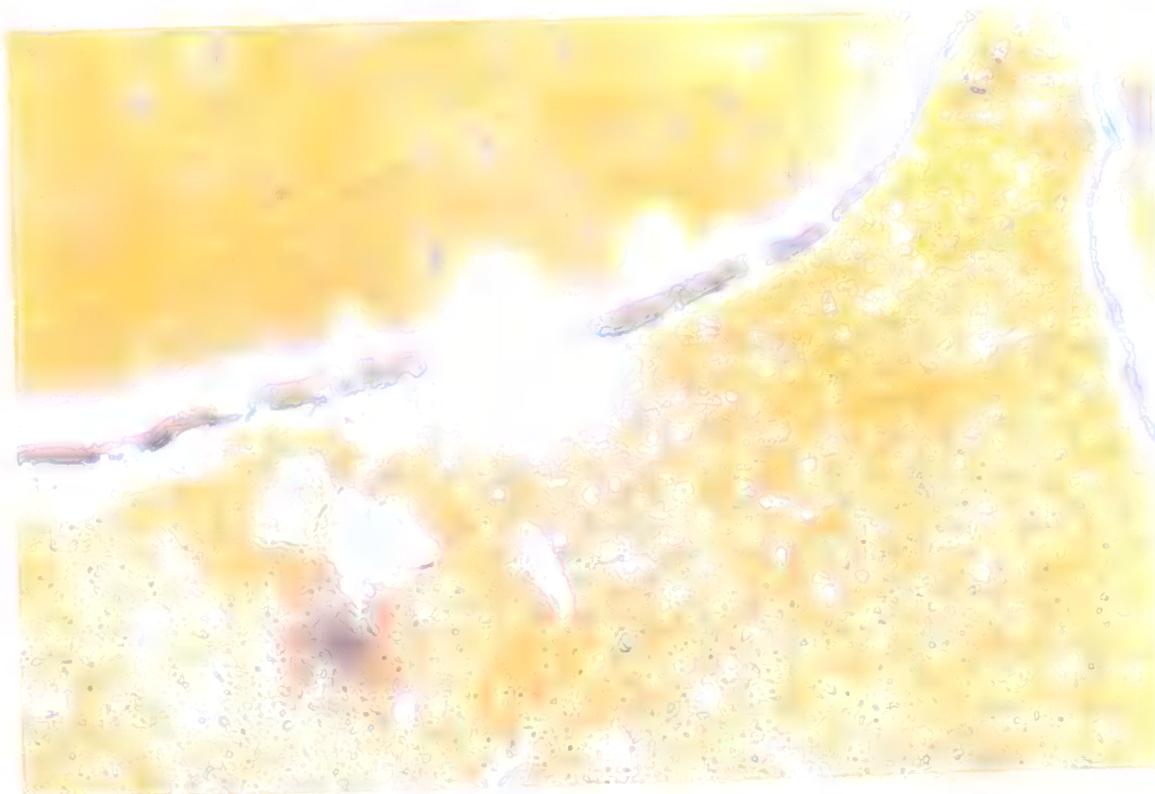


Plate 6.4

H63 x 200 Magnification Conditioned

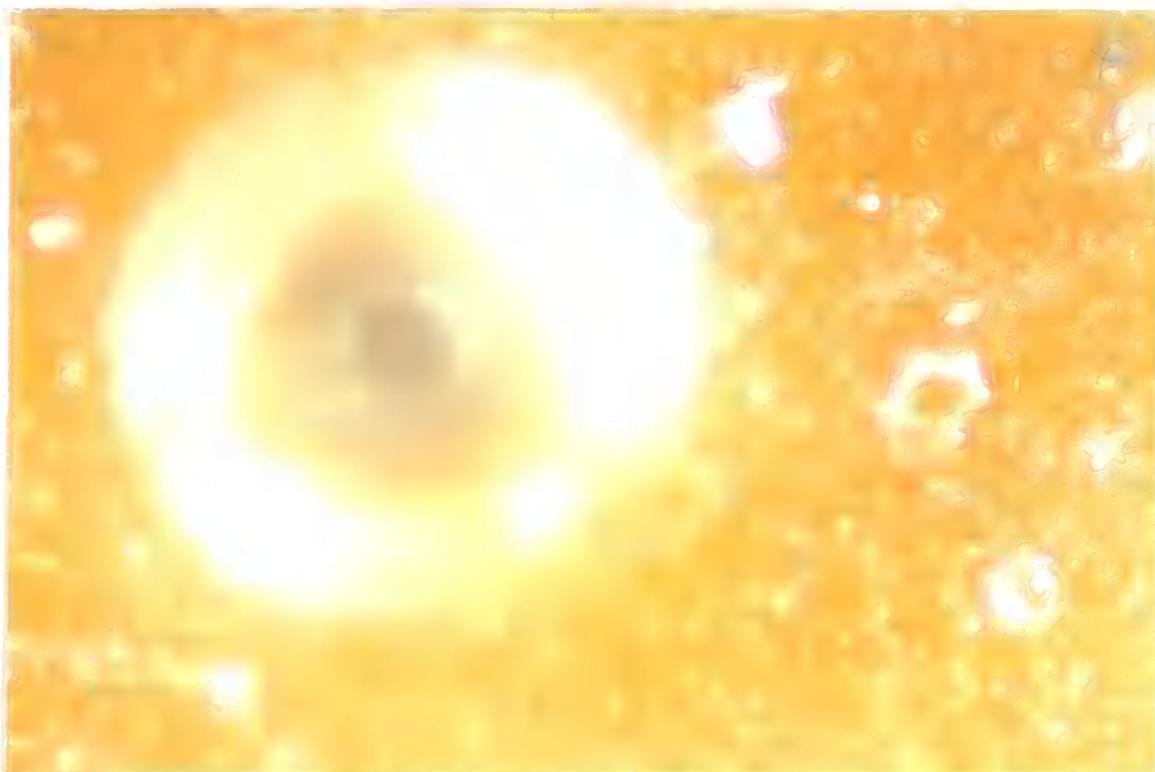


Plate 6.5

H62 x 200 Magnification Original

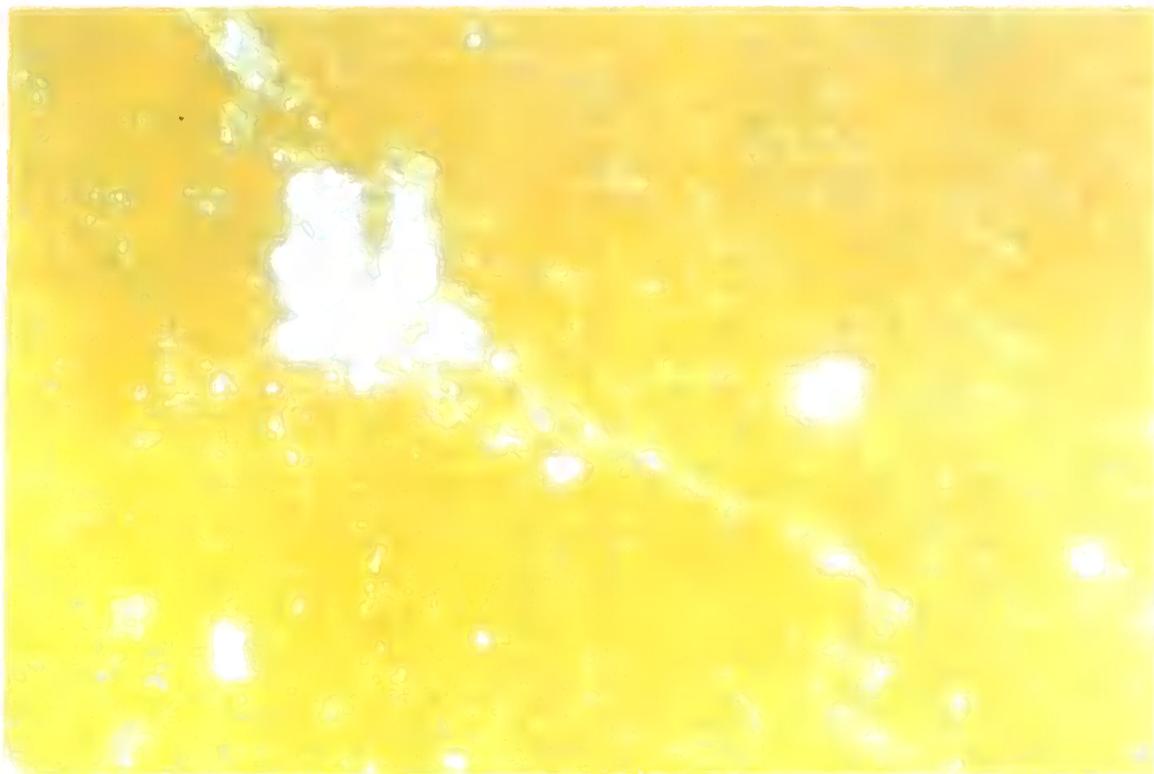
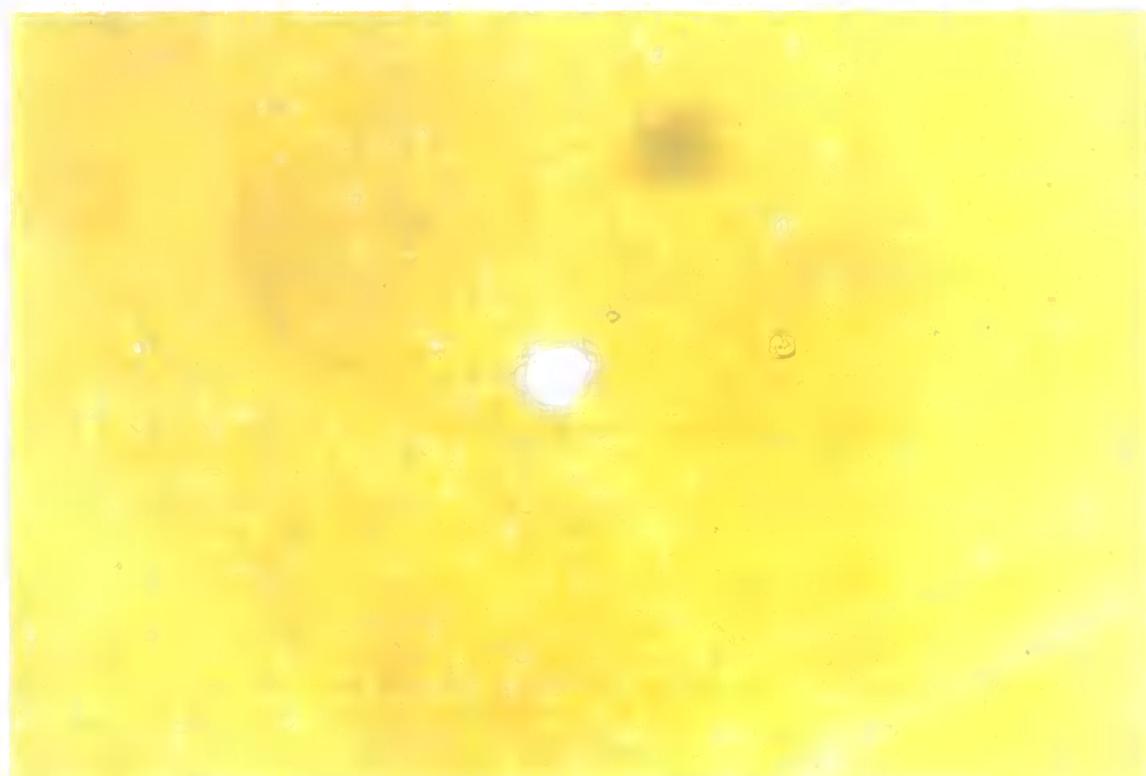


Plate 6.6

H62 x 200 Magnification Conditioned



6.5 Electron Microscopy

To characterise further the membranes evaluated in section 6.4.1, examination was continued with the use of a scanning electron microscope (SEM) (JSM 6100 Joel Japan). An electron beam current of 10KV was found to give the best results. The individual membranes were coated with a thin layer of gold (1 to 5nm). Electron probe microanalysis was completed using the energy dispersive X ray analyser (EDXA) (Link Analytical, High Wycombe, England) using an electron beam current of 25KV to ensure excitation of bromine. A light element window was fitted and was capable of detecting X-ray emissions from elements with an atomic number of 5 (boron) and greater. From purely theoretical considerations, detection of nitrate by either nitrogen or oxygen would appear feasible. In practice, this was not possible because of the reabsorption of the nitrogen X-ray emission by carbon and the ubiquitous nature of oxygen.

6.5.1 SEM Micrographs

Micrographs were prepared for the membranes evaluated in section 6.4.1 and are shown in plates 6.7 to 6.10. Micrographs could be taken using a beam current of 10 KV which reduced the level of sample charging. To perform satisfactory EDX analysis a beam current of 25 KV was selected. This ensured excitation of bromine and hence detection of the emitted X-rays. As an approximation at this setting, elements with an atomic number of 2.5 times the KV could be detected. Compositional examination of the surface particles for all the membranes produced similar results. The particles were composed of C, O, Na, Cl and K. These particles were confirmed as impurities from the polymerisation process [120]. It was proposed that the impurities from the polymer

Plate 6.7

H60 Original

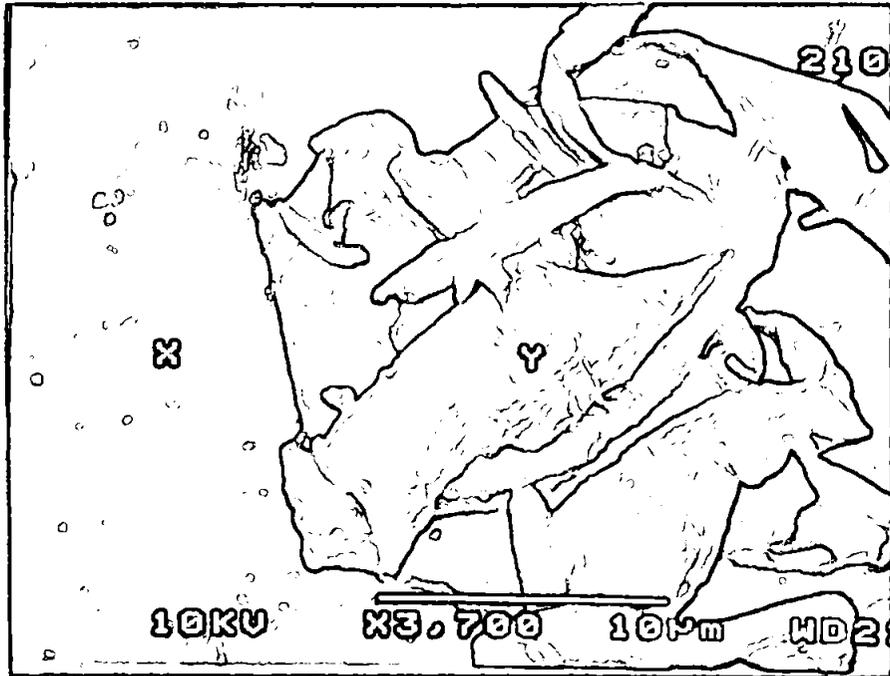


Plate 6.8

H60 Conditioned

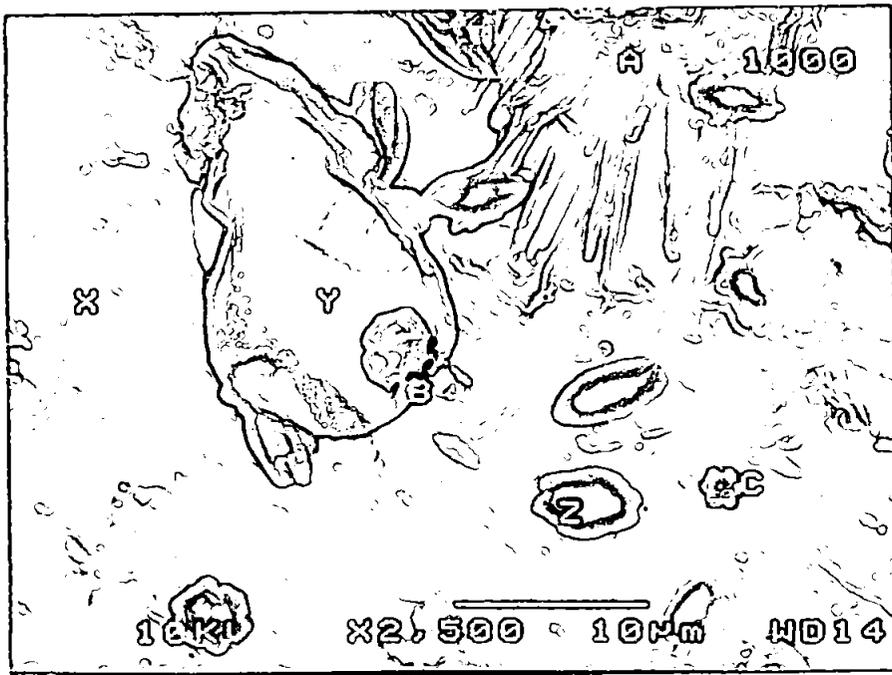


Plate 6.9

H63 Original

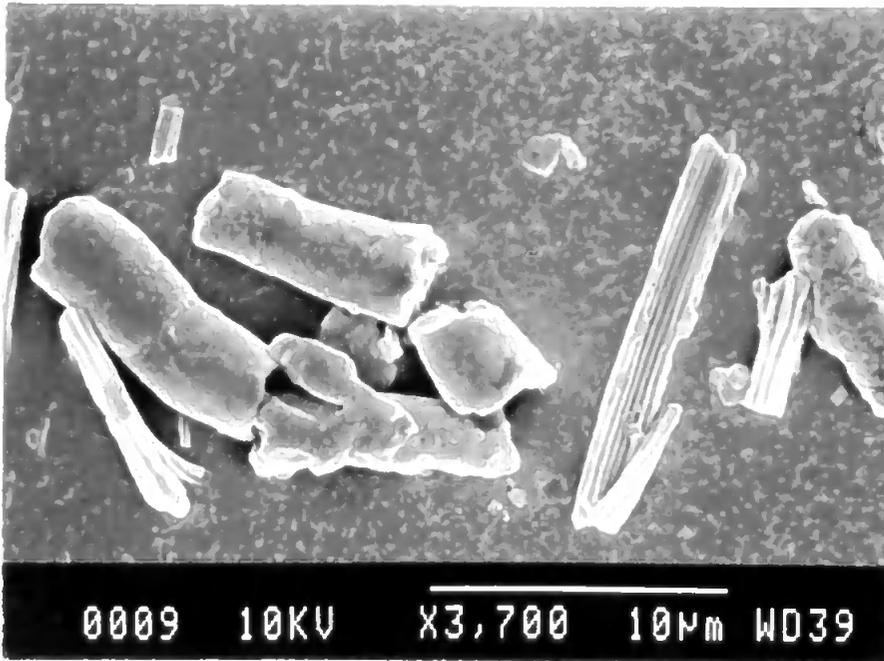
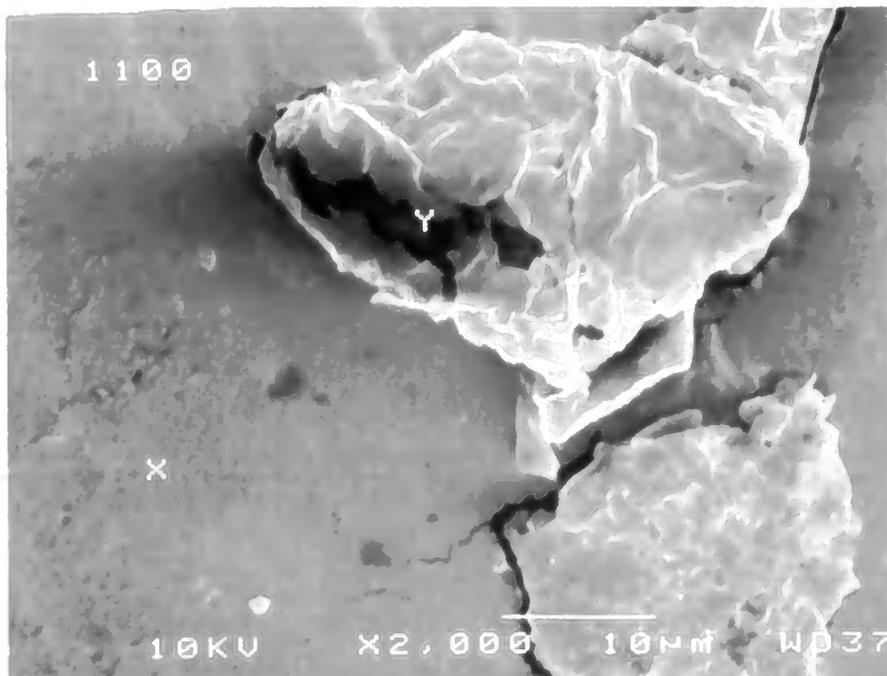


Plate 6.10

H63 Conditioned



had nucleated on the membrane surface to form particles between 2 and 10 μm in size. The impurities on the membrane surface were not expected to play any role in the development of the membrane potential. EDX analysis of the membrane surface for both H60 and H63 confirmed the presence of bromine from the added ion exchanger. The ion exchange process of bromide for nitrate during the conditioning process could not be monitored because of the reabsorption of the nitrogen X-ray emission. The absence of potassium from the membrane surface after conditioning was considered most significant since this reaffirmed the permselectivity of the membrane.

Interestingly, a recent paper [25] attributed similar particles observed in poly (vinylchloride) (PVC) membranes, to poorly dispersed agglomerates of ion exchanger. However the authors of that paper did not support their claims with compositional information of the particles by the use of EDX analysis.

6.5.2 Energy Dispersive X-ray Analysis

Although it was not possible to monitor the increase in nitrate during the ion exchange process, it was however possible to record the change in emission intensity for bromine. The results are only semi-quantitative since both the sample composition and sample preparation are known to affect the intensity of X-ray emission. Readings were recorded 1, 5, 10 and 20 μm into the membrane by examination of a freshly cut face. Results are shown in Table 6.12.

Table 6.12

Counts per Second for Bromine in NBR Membranes

Membrane Number	Distance from membrane surface/ μm			
	1	5	10	20
HP60 original/ counts per second	330	200	200	170
HP63 original/ counts per second	1200	1000	850	630
HP60 conditioned* /counts per second	1000	100	140	100
HP63 conditioned* /counts per second	30	420	140	100

*conditioned in 10^{-1} M potassium nitrate solution for 3 months.

The results although semi-quantitative illustrate a major difference in the behaviour of the two membranes. The compositional difference between H60 and H63 is that the latter membrane contained the solvent mediator 2-NPOE. The longlife membrane H63 had very little bromide at the surface which we presume to be due to ion exchange with nitrate. The electrode potential therefore arises from ion exchange involving a predominantly quaternary ammonium nitrate form on the membrane surface. The developed charge is then transferred through the bulk of the membrane. The extent of bromide replacement was influenced by the solvent mediator 2-NPOE which appeared to improved selectivity of the membrane HP63 for nitrate. These results are in agreement with the observations for ion exchange in section 6.1.3 where two possible process were proposed for the role of the solvent mediator. The EDXA results were

performed on both original and conditioned membranes. These membranes were conditioned for a period of 100 days and this was considered sufficient time to enable equilibrium conditions to be reached. Therefore, these results suggest that the solvent mediator 2-NPOE has improved the membrane selectivity for nitrate over bromide. For the shorter lifetime membrane H60, the relatively high level of bromide near the conditioned membrane surface is most surprising. The predicted reduced diffusion of anions within the membrane bulk would be expected to have quite the opposite effect and favour a reverse concentration gradient. The role of the counter ion in this case is important to enable a fuller understanding of the processes involved.

Membranes H60 and H63 were conditioned for 1 month in 10^{-1} M potassium chloride solutions because the presence of chlorine was readily detected by EDX analysis. Both original membranes and those previously conditioned for 3 months in potassium nitrate solution were evaluated. There was not any detectable chloride at the conditioned membrane surface and this supports the observed selectivity of the membranes for nitrate in the presence of chloride.

CHAPTER 7

Conclusions and Suggested Future Work

7.1 Solvent Casting Fabrication Technique

7.1.1 Studies with Poly (Styrene-b-butadiene) Matrix Membranes

Solvent cast membranes were fabricated using poly(styrene-b-butadiene-styrene) (SBS) as the polymer matrix. The work extended that of King [85] and found similar response properties with relatively poor nitrate selectivity. After appropriate conditioning the membranes gave a sub-Nernstian response to chloride, bromide and perchlorate solutions. The best SBS membrane fabricated was SBS E prepared using tert. butylhydroperoxide 11.8%*m/m* (14.7pphr) and contained triallylethylammonium bromide 8.2%*m/m* (10.2pphr). This membrane when appropriately conditioned gave a Nernstian response to nitrate of $-57.1\text{mV decade}^{-1}$ and a $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ value of 2.1×10^{-1} .

7.1.2 Studies with Poly (Acrylonitrile-butadiene) Polymer Matrix Membranes

The straight replacement of the SBS polymer matrix by poly (acrylonitrile-butadiene) (NBr) resulted in a significant improvement to the nitrate selectivity. The best solvent cast NBr polymer matrix membrane was more difficult to identify since a range of compositions gave rise to nitrate selective electrodes with a Nernstian response. For a combination of electrode response, limit of detection and selectivity coefficient, membrane C7 was the best composition and contained triallylbutylammonium bromide 9.4%*m/m* (11.9pphr), TBHP 11.6%*m/m* (14.7pphr) in a 50% ACN content polymer

matrix. This membrane produced nitrate selective electrodes with a Nernstian response of $59.2\text{mV decade}^{-1}$, limit of detection of $2.5 \times 10^{-5}\text{M}$ with respect to nitrate and a $k_{\text{NO}_3^-}^{\text{pot}}$, Cl⁻-value of 1.3×10^{-2} . The membrane was characterised by solvent swell measurement and was found to have a cross-link density of 1.8×10^{-5} mol cross-link cm^{-3} . In view of the relatively high level of free radical initiator used the number of cross-links was considered to be somewhat lower than expected. A similar attempt to characterise the SBS membranes revealed a low cross-link density especially at the membrane surface. This was believed to be due to the solvent casting fabrication method and choice of TBHP as the free radical initiator. The presence of oxygen at the membrane surface may have quenched the free radicals and hence prevented cross-link formation.

7.1.3 Disadvantages of Solvent Casting

It was not possible to incorporate solvent mediators into the membrane composition using the solvent casting fabrication method because of the relatively low cross-link density. The solvent mediator further softened the membrane producing very elastic materials which lacked physical strength. The solvent casting technique was therefore considered suitable only for membrane compositions which did not include a solvent mediator. The membrane thickness was very variable and a significant two sided response was noted. The two sided response characteristic was very undesirable and may have been caused by the previously mentioned oxygen quenching of the free radicals at the membrane surface, or the slow evaporation of solvent leading to concentration gradients in the membrane.

7.2 Hot Pressing Fabrication Technique

Because of the identified problems with cross-link density, two sided response and variable membrane thickness, an alternative fabrication method was sought. The development of the hot pressing technique produced membranes which were cross-linked, of a controlled thickness and did not display the undesirable two-sided response characteristic. The hot pressing method had the benefit of easily eliminating oxygen from the membrane environment. For an organic peroxide initiated reaction this was essential to prevent scavenging of the free radicals by oxygen.

The high temperature (150°C) associated with hot pressing was above the activation temperature of the organic peroxide and should therefore have been very effective in generating free radicals. When TBHP was used as the free radical initiator, hot pressing did not in itself increase the level of cross-links which remained at 1.3-1.8 mol cross-link cm⁻³. The best membrane fabricated using TBHP as the free radical initiator was membrane H1 which contained TABAB 9.3% m/m (11.9pphr) and TBHP 11.6% m/m (14.7pphr). This membrane produced a nitrate selective electrode with a response of -54.6mV decade⁻¹, limit of detection of 3.1 x 10⁻⁵M and a $k \frac{pot}{NO_3^-}, Cl^-$ value of 1.1 x 10⁻². Attempts to incorporate a solvent mediator into the composition were unsuccessful either because of lack of physical strength or poor response characteristics.

7.3 Dicumyl Peroxide as the Free Radical Initiator

The relatively low cross-link density compared to the level of organic peroxide used was therefore associated with the actual choice of TBHP. Stoichiometric replacement

with dicumyl peroxide resulted in hot pressed membranes with a cross-link density up to 8.07×10^{-5} mol cross-link cm^{-3} . This was sufficient to enable the introduction of a solvent mediator up to 65% m/m (233.4pphr) and yet still provided a robust membrane. Of the solvent mediators evaluated, the use of 2-nitrophenyloctyl ether in H12 gave the best response of $-58.4 \text{ mV decade}^{-1}$, limit of detection of $3.0 \times 10^{-5} \text{ M}$ and a $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ value of 1.2×10^2 . Electrode lifetime was extended from weeks to in excess of 4 months. Membrane H12 contained TABAB 5.6% m/m (11.9pphr), DCP 7.3% m/m (15.5pphr) and 2-NOPE 39.5% m/m (83.4pphr). For a number of different membranes, both with and without solvent mediators, there was little effect on selectivity coefficients for a range of common anion interferents. The values were found to compare very favourably with a commercially available PVC matrix nitrate selective electrode. We could conclude therefore that the lipophilicity or dielectric constant of the 50% ACN polymer was already sufficient to give satisfactory selectivity for nitrate.

The use of 34% ACN and 19% ACN content NBr as the polymer matrix required the use of a solvent mediator to provide a functioning membrane. The use of the 19% ACN content polymer in membrane H32 yielded the electrode which had the best overall selectivity coefficients. Membrane H32 had the same composition as H12 except that the 19% ACN content polymer was used. Although the membrane exhibited exceptional nitrate selectivity as shown by the $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ value of 1.1×10^3 it suffered from a very short lifetime of less than 2 months. This was believed to be due to the high level of unsaturation from the butadiene which resulted in predominantly polymer - polymer cross-links with reduced incorporation of the ion exchanger. In the 50% ACN content membranes, the lower level of unsaturation from

the butadiene therefore favoured the immobilisation of the ion exchanger via the unsaturated allyl substituents.

7.4 Cross-link Density Studies

The significance of cross-link density was investigated by the fabrication of a range of membranes with varying organic peroxide addition (from 2.8% m/m to 10.4% m/m). A good correlation between cross-link density and dicumyl peroxide addition was established within the range 0.6×10^{-5} to 11.0×10^{-5} mol cross-links cm^{-3} . There was no relationship between electrode response and cross-link density. The cross-link density did affect the selectivity coefficient for fluoride anions. Entry of the small anion into the membrane surface was restricted by an increase in cross-link density. The response mechanism for the nitrate selective electrode was concluded to be dependent on a surface layer ion exchange process followed by fixed site charge transfer across the membrane. It would be interesting to investigate the effect of a substantially greater membrane cross-link density on selectivity coefficients for a series of anions in the hope of yielding information about the mechanism of selectivity.

7.5 New Ion Exchangers

The ion exchangers triallyloctylammonium bromide (TAOAB) and triallyldodecylammonium bromide (TADDAB) were successfully synthesised. As predicted they resulted in an increase in hydrophobicity and the longer alkyl chains more closely mirrored the tetraoctyl and tetradodecylammonium nitrates used in commercial ISEs. The dodecyl derivative proved to have some compatibility problems

with the NBr due to the long alkyl chain and waxy nature of the QAS. The best electrode obtained from all those prepared in the course of this work was fabricated using a 50% ACN content polymer, TAOAB 6.5% m/m (14.0pphr), DCP 7.2% m/m (15.5pphr) and 2-NPOE 39.7% m/m (84.9pphr). This composition gave the longest lifetime membrane which continued to give a Nernstian response after 665 days. The electrode response was $-58.3\text{mV decade}^{-1}$, limit of detection of $4.5 \times 10^{-5}\text{M}$ and a $k_{\text{NO}_3^-, \text{Cl}^-}^{\text{pot}}$ value of 5.3×10^{-3} .

The use of 2-NPOE as solvent mediator did not significantly affect the selectivity coefficients of the TAOAB based membranes. It did however dramatically extend the electrode lifetime and therefore was regarded as having a critical role in the response mechanism. Most noticeably, 2-NPOE facilitated the response of an electrode in that it enabled a reduced level of ion exchanger to provide a Nernstian response. Chemical degradation of the immobilised QAS possibly by auto-oxidation would result in a reduction in active ion exchanger. Future work could investigate the role of degradation of the QAS possibly by the inclusion of established antioxidants such as butylated hydroxy toluene (BHT) in the membrane composition.

7.6 Role of the Polymer Matrix

A wide range of polymeric materials were evaluated as potential matrices and of these, the NBr polymers proved to be the best. From this work it was possible to summarise the desirable properties of a membrane matrix for use with immobilised ion exchangers and were as follows:

1. glass transition temperature below room temperature;
2. gumstock strength 6.9 MPa or greater;
3. compatible with polar solvent mediators;
4. contain a degree of unsaturation;
5. have a dielectric constant 4.5 or greater.

The dielectric constant was decided upon after reviewing values for a range of polymers, namely PVC (dielectric constant 4.55), SBS (2.55-2.95), NBr 50%ACN (4.5), NBr 34% ACN (3.8) and NBr 19%ACN (3.3) [121,122]. Interestingly, the NBr 50% ACN content polymer had the same dielectric constant as PVC whilst the other NBr polymers had lower values. This fits with the observation that a solvent mediator with a high dielectric constant was required for the 34 and 19% ACN content polymers to provide a functioning electrode. There are some exceptions to this requirement since SBS functioned as a membrane material with a lower dielectric constant but did have relatively poor selectivity. A polymer with a dielectric constant of 6.6, neoprene rubber was evaluated and proved unsatisfactory and this may imply some upper limit to the value. Future work could aim to test these properties and further refine the polymer requirements.

7.7 Glycine Betaine as an Ion Exchanger

Betaines are a class of naturally occurring quaternary ammonium compounds found in plants which are able to tolerate a high salt environment. When incorporated into a polymeric membrane they produced short lived membranes with a near Nernstian

response to nitrate. The short lifetime resulted from rapid dissolution of the betaine. It was not possible to covalently bond the water soluble betaine within the polymeric membrane using the free radical initiated immobilisation technique. The good selectivity coefficient $k_{NO_3^-, Cl^-}^{pot}$ of 4×10^{-3} exhibited by the membranes made it interesting to speculate as to the role of betaines in plant chemistry and the uptake of nitrates. Further work including certain organic synthesis could lead to the development of a novel ion exchanger. This would have to include immobilisation within the membrane to improve both electrode lifetime and limit of detection.

7.8 Mechanistic Studies

The use of quaternary ammonium salts such as TAOAB with a bromide counter ion necessitated a conditioning period in potassium nitrate solution to produce a nitrate responsive electrode. This process took up to 7 days to effect and was found to be rate limited by diffusion of the nitrate and bromide anions within the membrane.

The electrochemical behaviour of membranes both with and without a solvent mediator were markedly different. During the conditioning process, the solvent mediator increased the diffusion within the membrane and therefore accelerated the conditioning process. Typically these diffusion coefficients in a non-plasticised NBr membrane are of the order of, $10^{-10} \text{cm}^2 \text{s}^{-1}$ [123]. For a highly plasticised PVC membrane as used for ion selective membranes, diffusion coefficients as high as $5 \times 10^{-8} \text{cm}^2 \text{s}^{-1}$ may be expected [124]. With the NBr cross-linked membranes with immobilised ion exchangers we observed two characteristic responses: (a) with non-plasticised

membranes the response was more akin to a fixed site electrode; (b) as solvent mediator is introduced and diffusion became a dominant property so the response characteristics move closer to that of plasticised PVC membranes.

The inclusion of a solvent mediator in the membrane composition did not significantly affect selectivity coefficients $k_{NO_3^-, X^-}^{pot}$ - where X^- was a range of common anion interferents. Interestingly, the solvent mediator 2-NPOE did influence the ion exchange of bromide for nitrate during the conditioning process. The solvent mediator increased the selectivity of the membrane for nitrate in preference to bromide. The observation fitted established thinking for the role of a solvent mediator in a conventional PVC membrane electrode.

The use of the ion exchanger already in the nitrate form, made the conditioning process rapid and comparable to that for PVC matrix electrodes. The surface of each membrane required only to be hydrated before a response resulted and this was achieved within 24 hours. The effect of the nitrate form on the cross-linking reaction and hence, membrane properties and electrode lifetime was not fully evaluated. Concern had existed as to the effectiveness of cross-linking and immobilisation of the ion exchanger in the nitrate form. The full characterisation of these membranes is required with its impact on selectivity, electrode lifetime and membrane properties such as cross-link density.

Attempts to determine the level of immobilised ion exchanger did produce results, however, the method using solvent extraction could not be validated. This work illustrated the well known difficulties of extracting a polymeric matrix. The choice of

UV detection required significant changes to the membrane composition such that the model membrane used for extraction was very different to that of the optimum membrane. The free radical initiator was changed from dicumyl peroxide to TBHP and the plasticiser omitted to prevent interference. In addition a QAS was synthesised with the alkyl group replaced by the benzyl group although the three allyl substituents were unchanged. Further work should be aimed at developing and validating an analytical method to quantify the level of cross-linked ion exchanger within the matrix. The preferred membrane composition could be optimised to give maximum immobilisation and the effect on membrane lifetime established.

The use of electron microscopy provided valuable information about the polymer matrix. The myriad of small particles on the membrane surface could, easily be observed using a visual microscope. These particles were confirmed as impurities from the polymerisation process although the role in membrane potential and ion exchange properties was not evaluated. Within the conditioned membrane, significant ion concentration gradients were observed. It was presumed that the nitrate concentration was the inverse of that of the bromide anion. For the non-plasticised membrane, a higher concentration of bromide was noted at the membrane surface to that of the bulk, whereas the reverse was true for the plasticised membrane. Similar evidence for a membrane internal concentration profile [124] has been reported and in that case, was found to obey Ficks law. The difference in concentration profile between the plasticised and unplasticised membranes may be due simply to different diffusion characteristics.

The role of diffusion within the membrane appeared to be significant and would justify

further work. Experiments could be conducted to measure the diffusion coefficients in a range of membranes for various anions. There may be a relationship between diffusion coefficient and selectivity. The ease with which an anion can enter and possibly move or migrate within the matrix may be of paramount importance. Such work could aim to contribute toward an understanding of the relative importance of surface ion exchange mechanisms and the bulk transport or diffusion mechanism. The role of diffusion is also important in terms of whether anions migrate right across the membrane. Previous work [83] showed that cross-linked calcium selective SBS membranes were not permeable to calcium ions. The diffusion of nitrate anions across the membrane could be evaluated using an isotope of nitrogen. Because there is no suitable radioactive isotope (^{13}N has a short half life of 9.97 minutes) a stable ^{15}N isotope would be required. This could then be used in the $^{15}\text{NO}_3^-$ form and be determined using an isotope ratio recording mass spectrometer. Based on previous work we would now predict a difference in behaviour between the plasticised and unplasticised membranes. The plasticised membrane would be expected to perform in a similar manner to the standard plasticised PVC membrane and migration to occur across the membrane.

In this work we have developed a successful polymeric membrane nitrate selective electrode containing immobilised quaternary ammonium salts. Superior selectivity for nitrate has been recorded compared to conventional PVC membrane electrodes and an electrode lifetime in excess of 665 days reported. A greater understanding is needed of the mechanism of response and the critical factors influencing the electrode response. Such knowledge may enable electrode selectivity and lifetime to be optimised and so expand the use and application of ion selective electrodes.

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Appendix 1

Course of Study

Structured reading.

Conferences and Lectures Attended

Practical Chemical and Biological Sensors, The Royal Society of Chemistry, 9th to 10th December, 1987.

SPC and Total Quality, Plymouth Polytechnic, H. Coulson, December, 1987.

Flow Injection Analysis - The First Decade, Plymouth Polytechnic, Prof. A. Townshend, 29th January, 1988.

Diffusion in Polymers and Ultra Thin Membranes, University of Reading, 22nd to 24th March, 1988.

Research and Development Topics in Analytical Chemistry, Plymouth Polytechnic, 18th to 19th July, 1988.

Total Quality Management, Plymouth Polytechnic, Dr J. Pimblott, 7th December, 1988.

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