Development of ion-selective electrodes based on organic salts

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DEVELOPMENT OF ION-SELECTIVE ELECTRODES
BASED ON ORGANIC SALTS

by

ABDUL AZIZ AL-SIBAAI

A thesis submitted in fulfilment of the requirements for the award of Ph.D. of the Loughborough University

Supervisor : Dr. A. G. FORG

Department of Chemistry
Loughborough University of Technology

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DEDICATION

This thesis is respectfully dedicated to

My Mother

for without her encouragement over the years none of this could ever have been achieved.
ACKNOWLEDGEMENT

I would like to thank my supervisor, Dr A G Fogg for his stimulating help, guidance, invaluable suggestions and encouragement during the period of my study.

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My thanks are also due to Mr S N Jones for carrying out some of the experimental work on the mercury and surfactant electrodes under my guidance.

Finally, I thank all my colleagues for the very pleasant and unforgettable time that I have had with them at Loughborough.
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Preparation and use of the liquid-state electrode
The present work has been mainly concerned with the development of new liquid-state ion-selective electrodes. The electrode assembly used was based on a natural rubber membrane with electrical contact being made by means of a graphite rod at the back of the membrane. This assembly was used to study the response obtained with organic salts which are soluble in organic solvents. The hexachloroantimonate and tetrachlorothallate salts of Severon Red L, Severon Red G, Flavinduline 0, and phenazinduline 0 have been applied in these electrodes for the determination of antimony and thallium. The slope of the potential versus pH graphs approach full Nernstian response in the range $10^{-5} \text{M}(\text{Sb})$ and $10^{-6} \text{M}(\text{Tl})$ to $10^{-2} \text{M}$. Safranine 0 tetrachloroaurate has been used for the determination of gold in the range of $2.5 \times 10^{-7} \text{M}$ to $2.5 \times 10^{-4} \text{M}$ gold. Electrodes based on Brilliant Green perrhenate respond to the perrhenate anion and the Brilliant Green cation. Tribromomercuric(II) and lauryl sulphate salts of Methyl Green have been applied in electrodes for mercury(II) and surfactant. Crystal violet tetrabromoindate and tetrachloroindate salts have been applied to the determination of indium(III) and iron(III). Basic dye-acidic dye salts have been applied to the determination of acidic dyes. For example, the Crystal Violet - 4(2-pyridylazo) Resorcinol and Crystal Violet-Solochrome Violet RS salts have been used for the determination of 4(2-pyridylazo) Resorcinol, Solochrome Violet RS and Orange IV. Brilliant Green 12-tungstosilicate has been used for preparing an electrode responsive to Brilliant Green cation.

In the preparation of these electrodes, the solvent and the
kind of natural rubber used have been carefully selected. The effect of the pH of the solution and of interfering ions on the response of the electrodes have also been studied as well as the useful life of particular electrodes. The potential-concentration slopes of these electrodes have been found to be stable for a reasonable length of time (e.g. at least 3 weeks) but the potential shifts in one direction and this depends on the particular salt, the rubber and the solvent used.

Some other electrodes have been studied but are not recommended for general use either because of the short life of the electrodes or because of the short useful response range.
INTRODUCTION

The announcement by Frant and Ross\(^{(1,2)}\) of Orion Research Inc. of the fluoride and calcium responsive electrodes in 1966-7 may be said to have aroused the interest in ion selective electrodes. These developments were the culmination of studies made by many workers. Back in 1906, Cremer\(^{(3)}\) observed that a potential difference was developed at a 0.02 mm thick glass membrane placed between two aqueous solutions. This was followed by further investigations made by Haber and Klemensiewic\(^{(4)}\) who concluded that the potential difference between the solutions changes with the change in hydrogen ion concentration. A more detailed study was made by MacInnes et al\(^{(5-8)}\).

Haber with his students also foreshadowed later developments in heterogeneous membrane electrodes and liquid-ion-exchange types\(^{(4,9)}\). The importance of calcium ion in biological fluids inspired Tendeloo et al\(^{(10-13)}\) to many attempts to seek a reversible calcium sensor, but this was not achieved by Ross\(^{(2)}\) until 30 years after Tendeloo's initial attempt\(^{(10)}\).

During the last ten years, a considerable number of electrodes responsive to a wide range of different cations and anions have been developed. The construction of these electrodes is not restricted to one particular material, shape, size or design.

The response of some ion-selective electrodes is very selective for one particular ion and is not affected greatly by other ions. The ideal case is a specific electrode which responds to a change in the
activity of only one ionic species. Such an electrode does not at present exist, and the reading given by any ion-selective electrode is influenced more or less by the presence of other ions. For this reason, the term ion-selective electrode is to be recommended over the term ion-specific electrode.

The classification of ion-selective electrodes is not yet uniform. It seems that classifying them into (a) solid-state, (b) heterogeneous, and (c) liquid-ion-exchange types, which is based on the form of the electrode fabrication, is no longer appropriate because some active materials can be used in all three of the above forms. The new classification is based on the type of active materials which can be broadly classified into

a. glass;
b. insoluble inorganic salts; and
c. organic exchangers and chelating agents which include (i) long chain ion-exchanger materials; (ii) complexing agents; (iii) organic radical salts; and (iv) neutral carriers.

Lastly, enzyme electrodes can be classified in one group. They used to be classified as permeable membranes and the gas sensing ones as semipermeable membranes but both permeable and semipermeable membranes have been used in constructing enzyme ion-selective electrodes. Liquid state enzyme ion-selective electrodes have been used as well.
Due to the rapid development of the field of ion-selective electrodes, a vast number of papers and reviews have appeared in the literature in a relatively short time. The most comprehensive reviews are those of Buck (14,15), Moody and Thomas (16), Koryta (17) and Covington (18). Also, two textbooks, "Ion-selective Electrodes", N.B.S. publication number 314, edited by R.A. Durst (19), and "Selective Ion-Sensitive Electrodes" by Moody and Thomas (20), are the main texts on the subject.
The glass electrode responsive to hydrogen ion was the founder member of the current family of ion-selective electrodes. The discovery of its response to the alkali metal ion, led to attempts to develop an electrode selective for these ions. It was found that the selectivity for different ions is controlled by the composition of the glass. A range of monovalent cation responsive electrodes has been produced selective to the alkali metal ions. In addition some glasses respond to ammonium, thallium and silver ions and to a much lesser extent to alkaline earth ions. Tendeloo and Voorspuij\(^{(21)}\) made their electrodes from lithium calcium alumino-silicate glasses of various composition. Some of these electrodes gave nearly theoretical slopes for the monocationic Ca\(^{2+}\) and Ba\(^{2+}\), although some instability is evident in the Ca\(^{2+}\) measurement. The utility of these electrodes presumably was not very good, because Tendeloo turned to other methods in his subsequent studies\(^{(13)}\).

Baker and Trachtenburg\(^{(22)}\) investigated the chalcogenide glass semiconducting electrodes which are claimed to show Nernstain response to Fe\(^{3+}\) and Cu\(^{2+}\). The electrode does not respond to Fe\(^{2+}\).

The literature of this field is very extensive and has been systematically evaluated by many authors in the book edited by Eisenman\(^{(23)}\).
INSOLUBLE INORGANIC SALTS

The basic requirements of this type of material appear to be a low solubility, chemical inertness, mechanical stability, good electrical conductivity and the ability to equilibrate very quickly with the ion to be measured in the sample solution.

It seems to be preferable in order to obtain good performance to use this material as a compact disc or a single crystal where possible. A single crystal of LaF₃ with low electrical resistivity, which can be further reduced by doping the crystal with a divalent cation such as Eu²⁺, was used in the first ion selective electrode for the determination of fluoride which was described by Frant and Ross(1). The performance and the application of the lanthanum fluoride electrode are the subject of a vast number of papers.

The sulphide membranes of the Orion, Coleman and Beckman companies comprise silver sulphide. The dense, non-porous membrane of considerable insolubility has very low detection limit, good resistance to oxidizing and reducing agents and high sensitivity to both silver and sulphide ion.

When it is difficult to fabricate a single crystal or compact disc of pure material, an additive may be incorporated with the active material. For example, silver halides suffer from the serious photoelectric effect and have high electric resistance. However, a matrix(24) incorporating silver sulphide, which can be considered to be chemically inert here due to its low solubility product, provides a highly suitable
electrode material for determination of halide ions.

In a similar way, from a mixture of the sulphides of copper, lead or cadmium with silver sulphide, membrane electrodes can be produced that are responsive to $\text{Ca}^{2+}$, $\text{Pb}^{2+}$ or $\text{Cd}^{2+}$ (25).

Ceramic electrodes can be made by an annealing process. Hirata and Higashiyama described a number of them. The copper (I) electrode (26) was prepared by compressing a copper(I) sulphide at 150 kg cm$^{-2}$ to form a tablet which was heated at 500 - 900 °C for 1 - 5 hours in an atmosphere of hydrogen sulphide or nitrogen. In the same way, an electrode selective to lead(II) (27) was prepared by mixing thoroughly the desired amount of lead, silver and copper sulphide. Similarly, an electrode selective to $\text{Ag}^{+}$ was prepared by Liteanu et al. (28). Hirata and Higashiyama (29) later compared compact pellets with sintered ones which were prepared from a mixture of lead selenide or telluride and silver sulphide. They concluded that the compacted membranes with both selenide and telluride provide much poorer sensitivity than the sintered ones as well as having an inferior response rate and stability. The selenide or telluride sintered membrane electrode is rather better than the lead sulphide, silver sulphide sintered membrane as the useful range is from $10^{-1}$ to $10^{-7}$ M of lead(II) with 29.5 mV/p$\text{Pb}^{2+}$. Electrodes prepared similarly have been described (30) for silver, chromium(III), nickel, cobalt(III), cadmium, zinc, copper(II) and manganese(II) ions.

The inorganic active material may be incorporated in an inert binder material, which gives the membrane the required mechanical
properties. The inert binder must be chemically inert, hydrophobic, flexible, crack resistant and must not swell in the sample solution. These membranes are known as heterogeneous membrane electrodes, and a vast number of membranes has been prepared in this way. The inert binder may be silicone rubber (31-33) or polyvinyl chloride (34). The correct ratio of active material to binder must be achieved to ensure contact between particles to facilitate electrical conduction. Other important factors include the particle size of active materials, adhesion and cross-linking of the binder.

Lastly, the inorganic active material may be dissolved in an organic solvent from which a liquid membrane electrode is prepared. Ruzicka and Rald (35) constructed an iodide selective electrode from a porous graphite rod, impregnated with a solution of iodine in carbon tetrachloride, benzene or mesitylene, in a Teflon tube. Stainless steel wire was screwed into the graphite rod serving as a lead to the pH meter. The electrode is suitable for determining iodide down to $10^{-6}$ M. It has a selectivity constant over bromide of $10^{-3}$ and is not sensitive to light but is affected by reducing agents.
ENZYME ELECTRODES

In most of the applications of enzyme electrodes, the immobilized enzyme has been placed over an ion-selective electrode membrane using a polymeric gel. This gives an electrode highly selective or specific to certain organic molecules. Electrodes have been developed, for example, for the determination of urea, amino acids, glucose, amygdaline, penicillin and for assay of serum cholinesterase.

Guilbault and Harbankova have compared liquid type enzyme electrodes and those composed of polymerized ion for the determination of amino acids. They concluded that the latter was less stable and had lower response, probably because of partial decomposition of enzyme during the polymerization procedure. They pointed out that riboflavin, which was added to the gel solution as catalyst, is an inhibitor for amino acid oxidase. The liquid membrane needed one hour of conditioning and the polymerized membrane needed to be left overnight.

Guilbault and Stokbro recently proposed a new concept for determining urea. The enzyme was placed on the surface of a magnetic stirrer forming one unit, that both stirs the solution and catalyzes the enzymatic transformations in one step. The stirrer was stable and economical being useful for several hundred assays, and permitted very fast assays in a highly accurate and reproducible manner. The ammonia liberated is measured with an air-gap electrode specific for ammonia.
GAS SENSING ELECTRODES

The range of possible application of these electrodes is far from being recognised yet as it is not only gases (e.g. NH₃, SO₂, H₂S and NO₂) which can be estimated. A number of species in solution, or even in solid samples, which can be selectively and quantitatively converted to a gas may be sensed. For example, ammonia electrodes have been used for determination of ammonia, urea, or amino acid in serum or blood, and for the determination of nitrate.

Most of the electrodes used have the following features. The sensing element is covered with a thin membrane, made for example of rubber, polyethylene or other plastic materials, which separates the sensing element from the solution. High molecular weight substances, colloids, ions, and, to a certain degree, the solvent, cannot penetrate through the membrane while gases and some volatile substances can diffuse through to the surface of the sensing element. Between the sensing element and the membrane there is a thin layer of electrolyte in which the gases dissolve and are detected by the sensor.

A newly developed membrane material, a microporous Teflon, is made in such a way that up to 60% of its area consists of narrow pores filled with air. Thus the actual transport of gas from the sample to the inner electrolyte solution occurs through air rather than via solid material as was the case in the original membrane. The result is a much faster electrode response, as, according to Ross (47), the ratio of the DK values between air and dimethylsilicone rubber are:
<table>
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<th>Gas</th>
<th>Concentration</th>
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<tr>
<td>(O_2)</td>
<td>(3.6 \times 10^4)</td>
</tr>
<tr>
<td>(CO_2)</td>
<td>(5.5 \times 10^3)</td>
</tr>
<tr>
<td>(H_2S)</td>
<td>(2.3 \times 10^3)</td>
</tr>
<tr>
<td>(NO_2)</td>
<td>(2.2 \times 10^3)</td>
</tr>
<tr>
<td>(SO_2)</td>
<td>(9.7 \times 10^2)</td>
</tr>
<tr>
<td>(NH_3)</td>
<td>(5.4 \times 10^3)</td>
</tr>
<tr>
<td>(H_2O)</td>
<td>(26)</td>
</tr>
</tbody>
</table>

(\(D\) is the diffusion coefficient and \(K\) is the partition coefficient of the gas between the membrane material and the aqueous sample.)

The next factor influencing the speed of response is the electrode geometry described by the thickness of the electrolyte layer and the membrane material as well as by the effective electrode area.

By removing the porous membrane entirely, the last two factors are eliminated but the electrode has to be situated above the sample solution, so that it becomes separated from it by an air gap. Although the width of the air gap is larger than the hydrophobic membrane, the speed of the response of the air gap electrode is faster because the diffusion of the gas across the air gap is not hindered and the layer of the electrolyte is kept very thin. The advantage of the air-gap electrode is the ready and easy renewability of the electrolyte layer but the electrode must not touch the sample solution. Ruzicka et al.\(^{(48,49)}\) described a \(CO_2\)-air-gap electrode. Guilbault and Tarp\(^{(50)}\) described air gap electrodes specific to ammonia which have been used later in the determination of urea\(^{(46)}\). The ammonium content in waste water has been determined by means of the air-gap electrode\(^{(51)}\) as well as the hydrosulphite content of urine\(^{(52)}\).
ORGANIC ACTIVE MATERIALS

The common feature of these substances is their ability to bind certain ions selectivity, either at either charged sites of opposite sign or at neutral sites of an organic nature or in some cases at co-ordination sites. The simplest materials used are salts of long chain organic acids, such as oleates, ring substituted salicylates, or of organic bases such as the tetraalkylammonium salts.

The various organic salts, which have been used in ion-selective electrodes, namely di-alkylphosphates, tetraalkylammonium salts, phenanthroline complexes, organic radical-ion salts, tetraphenylborates, basic dye complexes and neutral carrier will be reviewed below. The method of electrode construction used in applying these materials will be mentioned briefly.
DI-ALKYLPHOSPHATE SALTS

Several di-alkylphosphates have been widely used for preparing electrodes selective to calcium but only a few for preparing electrodes selective to other ions. Dietrich and Manning (53) described an electrode selective to UO$_2^{2+}$ based on the UO$_2^{2+}$ salts of bis(2-ethylhexyl)phosphate incorporated in PVC matrix. The electrode can be used in NO$_3^-$, SO$_4^{2-}$ and F$^-$ solutions but not in CO$_3^{2-}$ and phosphate solutions. Electrodes based on UO$_2^{2+}$ complexes of bis(2-ethylhexyl)phosphate, bis(2-ethyl-4-methylpentyl)phosphate, or BuH$_2$PO$_4$ as ion exchangers exhibited nearly Nernstian response for UO$_2^{2+}$ in the range 10$^{-1}$ to 10$^{-4}$ M UO$_2^{2+}$ and were described by Manning et al (54). The active material was incorporated in a PVC matrix. Materova and Mukhovikov (55) used the strontium and barium salts of di-2-ethylhexylphosphate in chlorobenzene for strontium and barium liquid state electrodes.

The first important electrode based on calcium di-alkylphosphate was reported by Ross (2) for the determination of calcium ion. The calcium di-decylphosphate was dissolved in di-n-octylphenylphosphonate which saturates a millipore membrane. The membrane is held in the outer tube of the electrode body by an inner tube holding the internal reference solution. The space between the two tubes is used as a reservoir for the active material. The phosphate ion forms a stable complex with calcium but not with alkali metals. The long alkyl chain is necessary to prevent water solubility. The electrode mentioned above showed Nernstian response (29.4 mV/pCa) over the range pCa 1 to 5. The lower limit of detection is governed by the low solubility of
the calcium phosphate ester salt in the aqueous phase. The lower
detection limit can be improved by increasing the length of alkyl
chain but if this is too long, precipitation or gelling may occur.
Alternatively, the concentration of the active material can be
reduced but this has the effect of lengthening the response time \[^{25}\].
The electrode gave correct calcium activity readings between pH 5.0
and 11.0. Below pH 5.0 hydrogen ion interferes and CaOH\(^+\) and Ca(OH)\(_2\)
are formed above pH 11.0. Good selectivity was found for calcium
over magnesium and other alkaline earth ions but the electrode
responds also to Zn\(^{2+}\), Fe\(^{3+}\) and Pb\(^{2+}\). Some difference in selectivity
can be achieved by varying the solvent polarity. With 1-decanol, the
electrode showed virtually identical responses to calcium and magnesium,
this is the basis for the water hardness Ca\(^{2+}\)/Mg electrode \[^{25}\].
Moody and Thomas \[^{20}\] made an evaluative study of a number of com-mercial and non-commercial calcium selective electrodes. The liquid
type electrode, according to Moody et al \[^{56}\] produced an ill-defined
interface and the membrane offered poor mechanical resistance. The
slow leakage of the ion exchanger solution into the test solution
creates the danger of contamination of the test solution. They
incorporated tributylphosphate and didecylphosphoric acid in poly-
viny1 chloride (PVC). Further investigation of the optimum composition
of the matrix membrane was made \[^{57}\]. The membrane was affixed to a
recessed end of PVC tube with a solution of PVC in tetrahydrofuran
as adhesive. The tube was filled with the internal reference solution
which is in contact with the internal reference electrode. According
to Moody and Thomas \[^{20}\], the electrode is superior in life-time perform-
ance to any present commercial item and it is easily made. Beckman
workers \[^{58,59}\] dissolved either calcium didecyl- or dioctylphosphate
in ether-alcohol solution of collodion. The active organophosphate-collodion matrix remaining after evaporation of ether alcohol becomes the functional calcium sensitive membrane. Some workers eliminate the internal reference solution using several different techniques. Ansaldi and Epstein\(^{(60)}\) used the Orion No. 92-20-01 calcium liquid ion exchanger, of which the exact composition is not certain, for preparing a PVC membrane. The membrane was cemented to one end of Tygon tubing with a mixture of PVC in tetrahydrofuran. A graphite rod was force fitted into Tygon tubing. Good contact between the graphite rod and the membrane was indicated. The electrode was similar in performance to the liquid type described above. Ruzicka et al\(^{(61)}\) described a selectrode for calcium consisting of a porous Teflon graphite pellet containing a solution of calcium didecylphosphate in dioctylphenylphosphonate. The pellet was screwed to the electrode body which consists of Teflon tubing containing the pressed graphite hydrophobized by Teflon. Good contact between the pellet and the graphite was found. The Selectrode had a slope close to Nernstian and the sensitivity limit for calcium was down to pCa 6. Ruzicka et al\(^{(62)}\) also synthesized calcium di-n-octylphenylphosphate(DOPP) and compared electrodes based on this compound with electrodes based on calcium decylphosphate in liquid form or as PVC membranes. The PVC membrane was in direct contact with teflon-graphite surface after rubbing on the surface a paste of mercury-calomel-potassium chloride-calcium sulphate which forms a reference layer between the teflon-graphite body and the PVC membrane. The membrane was held in position by a Teflon cap screwed to the electrode body to ensure water tightness. The linear response range of the DOPP-PVC based electrode was from pCa 2 - 5.7 which is a significant improvement on the DDP based
electrode. The selectivity parameters towards foreign ions as measured over a seven week period remained unchanged and the electrode did not deteriorate in any respect.

Cattral and Freiser(63) coated platinum wire with a 6:1 mixture of 5% PVC dissolved in cyclohexanone and 0.1M calcium didecylphosphate in dioctylphosphonate. The wire was dipped in the mixture several times and allowed to set overnight in air. The remainder of the exposed wire was covered by wrapping it tightly with a paraffin film to prevent direct contact of the metal surface with the test solution. The coated wire electrode gives a very rapid response (10 - 15 sec), can be stored in air and has a long useful life (more than three months). Sapio et al(64) prepared the calcium electrode by making a paste from calcium didecylphosphate in dioctylphenylphosphonate and a commercial graphite powder. A 10 mm thick layer of the graphite paste was packed into one end of a glass tube around a platinum wire which was secured at the other end of the tuning with a rubber O-ring. No conditioning of the electrode is necessary but the drawbacks to the electrode are its sensitivity to stirring and the need for periodic re-standardization.

A vast number of papers have appeared in the literature concerning calcium electrodes and their application especially in biological analysis(65,66). Other major uses include the determination of ion activity coefficients, dissociation constants, stability constants of complexes and the determination of calcium in sea-water, detergents, soil, etc.(20,67). A divalent ion-selective electrode was used in an indirect method of determining tri- and tetravalent
ions (68). The determination is based on displacement of the divalent metal ion from the Mg-EDTA by tri- or tetravalent ions. La(III), Fe(III), Bi(III) and Zr(IV) have been determined in this way.
TETRAALKYLAMMONIUM SALTS

Tetraalkylammonium salts are another group of organic salts which have been widely used. The Corning liquid state nitrate electrode (18) was based on tridodecylhexadecyl ammonium nitrate in n-octyl-2-nitrophenyl ether. The principal interfering ions are ClO₄⁻, I⁻, ClO₃⁻ and Br⁻. Coetzee and Freiser (69) developed a series of anion responsive electrodes based on the tricaprylylmethyl ammonium (Aliquat 336) salts. Later (70) they studied the pH dependency and the effect of the interfering anions on the electrode response for sixteen of Aliquat 336 salts. The conclusion was that although the electrodes cannot be considered to be highly selective, a wide range of useful measurements can be made with them. Further studies (71, 72) showed that the selectivity ratio of the various electrodes varied from 10⁻³ to 10⁻¹ in a manner that seemed to follow from the relative extractability of the interfering ion. This was confirmed by comparison of competitive extraction constants and selectivity ratios in which an essentially linear relationship was obtained between the log K value for the extraction and electrode selectivity. Gibson and Weatherburn (73) studied the extraction of 14 quaternary cations with 19 anions into chloroform, dichloromethane, 1,2-dichloroethane and 2-2-dichloroethyl-ether. They concluded that for a given cation, the critical factor in the extraction was the enthalpy of hydration of the anion, changing from effectively 100% to virtually zero. The size of the cation had a secondary effect.

Aliquat 336 salts have been used in PVC matrix to coat platinum wire which results in electrodes selective to perchlorate,
chloride, bromide, iodide, thiocyanate, benzoate, salicylate, oxalate, sulphate, phenylalanine and leucine\(^{(74)}\). The electrodes were still functioning after three months of use and they can be stored in air. A graphite paste of Aliquat 336 chloride was used by Sapio et al\(^{(64)}\) as the active part of an ion selective electrode responsive to chloride. Matsui and Freiser\(^{(75)}\) prepared liquid membrane electrodes selective to phenylalanine, leucine, methionine and glutamic acid based on the appropriate salt of Aliquat 336 dissolved in decanol. Herman and Rehnitz\(^{(76,77)}\) claimed that their carbonate ion-selective electrode was highly selective to carbonate over chloride, phosphate and hydrogen carbonate with Nernstian response over a wide range of carbonate concentration \((10^{-2} \text{ to } 10^{-6} \text{ M})\). The electrode was based on Aliquat 336 carbonate dissolved in trifluoracetyl-P-butylbenzene. Tetraheptyl ammonium perchlorate was singled out as a promising C\(104^+\) electrode\(^{(18)}\) and the salicylate salt as a salicylate electrode\(^{(78)}\). The nitrate salt of tetraheptyl ammonium was used in studying the dependence of selectivity on organic salt concentration by Danesi et al\(^{(79)}\). They concluded that the choice of the liquid electrode concentration depends on the required value of the selectivity factor. Danesi et al\(^{(80)}\) also studied the behaviour of some electrodes based on tetraheptyl ammonium salts. They found that both the solubilization of alkylammonium salt in water and the change in the composition of the membrane phase are processes which contribute to the transient potential. By using aqueous solutions pre-equilibrated with the organic phase, the potential becomes independent of time. The iodide salt was used by Corning Glass Works\(^{(81)}\) in their early work on three different forms of electrode construction. The active material was dissolved in the organic solvent and the solution was used
to fill the bottom and extend upwardly a short distance in both arms of the U-tube. A standard Ag-AgCl electrode was immersed directly in the organic liquid to provide the electrical conductivity. The test solution was placed in one of the U-tube arms, and, in the other, an equal quantity of deionized water was placed to balance the test solution. Alternatively, the organic solution was placed in a tube ending with a membrane to provide mechanical support. The Ag-AgCl electrodes were immersed directly into the organic solution. Thirdly, a paste was made from the ammonium salt and sufficient colloidal silica using n-dedylalcohol as mediator. The paste was packed in one end of the tubing and the electrical contact was made by a metal lead contacting the paste. Birch and Clark (82) used cetyltrimethylammonium dodecylsulfate in nitrobenzene to prepare electrodes selective to the cetyltrimethylammonium cation and the dodecylsulfate anion. Further studies (83) showed that an improvement of the electrode performance was made by increasing the solubility of the complex in the organic solvent. This was done by addition of small amounts of a water-insoluble hydrogen-bonding solute. They found that the most satisfactory solvent was 0.17 M hexachlorobenzene in o-dichlorobenzene which was also 0.017 M in bromoacetanilide. The detection limit was $10^{-5}$ M. A silicone-rubber electrode responsive to cationic detergents, based on hexadecyltrimethylammonium dodecylsulfate, was described by Fogg et al (84). Nernstian response was over the range $10^{-3}$ to $10^{-5}$ M hexadecylpyridinium bromide and hexadecyltrimethylammonium bromide solutions. The electrode was used in the potentiometric titration of sodium dodecylsulfate, sodium tetraphenylborate, ammonium reineckate, potassium hexacyanoferrate(III) and potassium dichromate using hexadecyltrimethylammonium bromide as titrant. A
liquid state electrode selective to molybdenum was described by Fogg et al. (85). The electrode was based on bis-tetraethylammonium pentathiocyanatooxomolybdate(V) dissolved in nitrobenzene : O-dichlorobenzene (2:3). The electrode had Nernstian response over the range $10^{-2}$ to $5 \times 10^{-8}$ M molybdenum. Iron, vanadium, tungsten, niobium and rhenium, which form thiocyanate complexes, interfere. Stowrzewicz et al. (86) used solutions of octadecyldimethylbenzylammonium chloride or thiocyanate in chloroform or 1,2-dichloroethane in a simple electrode assembly for the determination of chloride and thiocyanate. A glass tube was closed at the bottom with a Teflon stopper. A hole through the stopper (0.5 mm in diameter) was fitted with a filter paper plug to act as the liquid membrane support. The organic solution wetted the plug and constituted a selective barrier. Above the organic solution was the internal reference electrolyte in which a reference electrode was immersed. The same active material in PVC was used as a coated film on a platinum wire. Back (87) used tetrahexylammonium picrate in methylene chloride for the determination of Cl$^-$, NO$_3^-$, Br$^-$, I$^-$ and ClO$_4^-$ . He confirmed the linear relationship between the selectivity ratios and the extraction ratios. The salts of tetradecyldimethylbenzylammonium or methyltricaprylammonium with the anion to be determined; ClO$_4^-$, SCN$^-$, 1-naphthalenesulphonate, H-phthalate or salicylate were used to prepare PVC membrane electrodes selective to the particular anion (88). The electrodes had high selectivity in the presence of acetate, bromide or chloride. A surfactant ion selective electrode was described by Rataoka and Kambara (89). The salt formed between benzyltetradecyldimethylammonium cation and dodecylbenzenesulphonate anion was extracted from the media into nitrobenzene. Naphthalene was dissolved in the hot nitro-
benzene solution and the resulting material which is solid at room temperature, was used to coat a platinum electrode. The response of the coated electrode was rectilinear in the range $10^{-3}$ to $10^{-7}$ M of dodecylbenzenesulphonate.
Another class of active materials used in anion-selective electrodes are the salts of the formula $ML_x^{n+}$ where $M$ is an ion such as $\text{Ni}^{2+}$, $\text{Fe}^{2+}$, $\text{Co}^{2+}$, $\text{Cu}^{2+}$ or $\text{Cd}^{2+}$ which complexes with a large neutral ligand, $L$. The metal ion in the complex must have a low rate constant for exchanging relative to that of the anion. Also the metal ligand complexes must be stable, i.e. will not hydrolyze or dissociate in contact with water. The complex must have a very low solubility in the aqueous phase, and must be able to conduct electricity. The Orion perchlorate electrode is based on iron(II) substituted 1,10-phenanthroline complex and the nitrate and tetrafluoroborate electrodes on the nickel(II) complex. Ishibashi and Kohara concluded that quaternary ammonium salts were slightly superior to the 0-phenanthroline complexes for determination of perchlorate. Reinsfelder and Schultz studied the selectivity of liquid membrane electrodes for common inorganic anion based on tris(1,10-phenanthroline) iron(II), tris(4,7-diphenyl-1,10-phenanthroline) iron(II) or tetrahepteylammonium salt in nitrobenzene, chloroform or n-amyl alcohol. With the exception of the amyl alcohol electrode, selectivity coefficients were relatively independent of membrane composition and followed a common sequency of decreasing selectivity: $\text{PF}_6^->\text{ClO}_4^->\text{SCN}->\text{I}^->\text{BF}_4^->\text{NO}_3^->\text{Br}^->\text{Cl}^-$. This sequence parallels the order of increasing hydration energy, suggesting that aqueous phase solvation energies play a predominant role in determining electrode selectivity for these ions. The equilibrium takes 30 minutes to be established when the electrode is transferred from one ion solution to another at the same concentration.
The Orion nitrate exchanger has been incorporated in PVC matrix to prepare a membrane electrode selective to nitrate\(^{(93)}\). After the electrode had been used in nitrate-perchlorate solutions, it took up to 40 minutes before returning to normal behaviour with pure nitrate solution. Hulanicki et al\(^{(94)}\) used tris(4,7-diphenyl-1,10-phenanthroline) nickel(II) nitrate in p-nitrocymene as active material for the nitrate electrode. The electrode consists of a wick made of natural or synthetic porous polymer which is saturated with a liquid active material. The back of the membrane is in direct contact with a platinum wire fixed in the wick. To increase the liquid exchanger capacity, the internal part of the wick is in contact with a chemically neutral porous foam soaked with the liquid organic active material. The electrode behaved in a Nerstian manner in the range \(10^{-1}\) to \(10^{-5}\) M of nitrate and the reproducibility was within \(\pm 0.5\) mV. Hazemoto et al\(^{(95)}\) used 4,7-diphenyl-1,10-phenanthroline ion(II) saccharate in nitrobenzene to prepare a saccharine liquid state ion-selective electrode. The electrode measured the saccharine ion concentration over the range \(10^{-1}\) to \(10^{-5}\) M of saccharine in the presence of other sweetening agents e.g. sucrose, glucose, sodium cyclamate and sorbitol. Jyo et al\(^{(96)}\) described electrodes selective to malic and phthalic acids based on salts of tris(bathophenanthroline) iron(II). The nitrate electrode has been widely used and studied as the determination of the nitrate content of water may give valuable information about pollution by decomposition of organic material or by nitrate fertilizers\(^{(97,98)}\). The electrode has been used for potentiometric titration using diphenyl-thallium(III) sulphate as titrant\(^{(99)}\). The electrode has been used in determining the nitrate in grass\(^{(100)}\) and a successful new technique
for the assay of nitrate reductase activity has been developed (101, 102). Perchlorate is of much less interest outside chemical laboratories where it is widely used. A potentiometric titration of perchlorate using tetraphenylarsonium chloride was followed using a perchlorate electrode (99, 103). Inflections are reasonably clear (104) with potential jumps of more than 100 mV. The electrode was used for the determination of vicinal glycols (105), (ethylene-, propylene- and butylene-glycols). The vicinal glycol was oxidised with periodate and the reaction rate was followed with perchlorate electrode. Orion fluoroborate ion-selective electrodes have been used for potentiometric determination of boron in silicon (106).
ORGANIC RADICAL-ION SALTS

The studies of Sharp and Johansson\textsuperscript{(107)} suggested that semi-conducting organic radical-ion salts may be used profitably as the active components of solid state ion-selective electrodes. As the organic radical-ion salts possess open-shell electronic configurations, they may exhibit acceptably low electrical resistivity in the solid state. Electrodes for silver, copper, tetraethylammonium and tetraphenylarsenium ions were prepared from the salts of 7,7,8,8-tetracyanoquinodimethane anion radical (TCNQ) and the cation in question. The ground salts were moulded into pellets, 8 mm in diameter and 1 - 2 mm thick, under pressure in the range of 10 - 20 tons cm\textsuperscript{-2}. The pellets were attached to a bright platinum base with graphite paste as adhesive and as electrical contact. All surfaces other than the responding one were insulated with plastic enamel. All the electrodes showed a Nernstian response over the concentration range limited by the solubility of the particular salts in the medium in question, around 10\textsuperscript{-5} M. Also the response time appeared to be determined by the solubility of the electrode material; the higher the solubility the slower attainment of equilibrium. Further studies by Sharp\textsuperscript{(108)} were made of electrodes made from lead, copper and tetraphenylarsenonium salts of 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (TNAP), 9-dicyanomethylene-2,4,7-trinitrofluorene DTF and 2,4,5,7-tetranitrofluorene-\(\Delta^9\),\(\sim\) malononitrile (TFM). All the above three compounds possess planar, aromatic molecules which are heavily substituted with the electron-attracting groups -CN and -NO\textsubscript{2}. Each molecule consequently shows high electron affinity and -delocalization of an acquired electron over the entire atomic framework lending
stability to the resulting radical-anion. The electrodes, prepared as mentioned before, functioned almost immediately on initial immersion in the test solutions. The response times were less than 3 minutes and pre-soaking was not required. \((\text{C}_6\text{H}_5)_4\text{As(DTF)}\) electrodes have been stored dry for 3 months without serious deterioration in electrode properties. The electrodes showed Nernstian response over the activity range \(10^{-1}\) to \(10^{-6}\) M. By comparison, a \(\text{Pb(TCNQ)}_2\) electrode showed a lower limit in its linear range. This supported Sharp's original assumption that by employing salts of a radical anion with a higher molecular weight as electrode sensors, lower solubility and a consequent improvement in operational range would result. A \((\text{C}_6\text{H}_5)_4\text{As(DTF)}\) electrode was used in potentiometric titration of perchlorate solution with solutions of \((\text{C}_6\text{H}_5)_4\text{AsCl}\). The encouraging results obtained with organic radical-anion salts as active substances in solid-state cation sensitive electrode led Sharp \((109)\) to the consideration of whether a similar approach might provide acceptable electrodes sensitive to anions. The first results obtained with perchlorate electrodes were encouraging as a good selectivity for perchlorate ion over some common anions was observed but linear Nernstian response covered the activity ranges \(10^{-1}\) to \(10^{-3.5}\) only in the pH ranges 3 - 5. The active materials were perchlorate salts of O-Tolidine, O-dianisidine and benzidine cation organic radicals. The Selectrode was used in the initial stages of his work. His later modification, which was constructed from PVC and commercial carbon-impregnated Teflon also functioned satisfactorily. Further studies \((110)\) showed that the perchlorate salt of N-ethylbenzothiozol-2,2-azaviolene gave a better response in the range \(1 - 10^{-4.8}\) M of perchlorate. The significant improvement has been reported when the
same radical ion salt was used in the liquid state form (111). The electrodes based on the same radical ion salt in 1,2-dichlorobenzene and in 8,8'-dichlorodiethylether responded to perchlorate in the ranges $1 \times 10^{-6.5}$ and $1 \times 10^{-5}$ M respectively. Short response time and acceptably stable potentials were observed for both liquid membrane electrodes. Both electrodes showed high apparent selectivities for perchlorate over hydroxide, nitrate, chlorate, sulphate, bromide, fluoride, acetate and chloride. Iodide and tetrafluoroborate were the most serious interference in each case. The low interference shown by hydrogen and hydroxide ions indicate that perchlorate determinations may be performed with the pH range 1 - 12 with both electrodes. Care is necessary in the choice of the solvent, particular attention must be given to the acid-base and redox properties of the solvent since these are major factors which affect the stability of a given radical ion species. As a general rule, high boiling point solvents of low permittivity which are devoid of functional groups such as -OH or -NH$_2$ are to be preferred. Gordievskii et al (112) described a membrane electrode for nitrate based on 1,4-diphenyl-3,5(endoani)-dihydro-1,2,4-triazole (nitron) nitrate in benzyl alcohol. The range over which the potential was linear was $10^0$ and $10^{-3}$ M of nitrate. The analytical value of the membrane is its selectivity to nitrate in the presence of large amounts of fluoride and phosphate ions. The cell used was constructed from two compartments containing the test solution and the standard one. The compartments are separated by a porous membrane saturated with the organic salt solution.
TETRAPHENYLBORATE SALTS

A few salts having the formula \((\text{C}_6\text{H}_4\text{X})_4\text{BA}\) have been used mainly for determining potassium, where \(\text{X}\) is hydrogen chloride or phenoxy and \(\text{M}\) the cation to be measured. Tendeloo and Krips\(^{(113)}\) tried potassium tetraphenylborate in heterogeneous membrane form as an electrode for potassium. Corning Glass Works\(^{(114)}\) have used potassium tetrakis(p-chlorophenyl)-borate in a solvent mixture of p-hexylnitrobenzene and 4-nitro-1,2-dimethylbenzene. Selectivity constant values of \(K^+/Na^+\) at \(10^{-4}\), \(10^{-3}\) and \(10^{-2}\) molar potassium salt solutions are 55:1, 80:1 and 90:1 respectively. Using 3-nitro-1,2-dimethylbenzene as a solvent, the selectivity for \(K^+/Na^+\) was 100:1. When sodium tetraphenylborate was used as the active material in decanol, the electrode was slightly more selective to sodium over potassium. Liquid state and PVC potassium electrodes have been prepared using potassium tetrachlorophenylborate in 2,3-dimethylnitrobenzene\(^{(115,116)}\). An electrode selective for acetylcholine was based on acetylcholine tetrachlorophenyl borate in either 3-0-nitroxyylene, dibutylphosphate or tri(2-ethylhexyl) phosphate\(^{(117)}\). The selectivity has been studied for acetylcholine in the presence of propionylcholine, butylcholine, valerylcholine, isobutyrylcholine and acetyl-(-methylcholine. A linear relationship was found between the selectivity factor and the free energy of transfer function. The solvent has a strong effect on the selectivity of the electrode.

Ishibashi et al\(^{(118)}\) described a liquid state vitamin selective electrode based on thiamine tetraphenylborate in dichloroethane. The electrode has Nernstian response over the range \(10^{-1}\) to \(10^{-5}\) \(\text{M}\) of thiamine.
A very important development has been the discovery and use of neutral carrier complexes selective towards alkali-metal and a few other ions. The neutral carriers are electrically neutral organic molecules which carry a sequence of localized charges (usually lone pair electrons) of sufficient energy to form ion-dipole ligands with selected cations. The conformation of the molecule is such that it wraps round the ion and, thereby, provides a cavity of the right size. The group includes the macrocyclic antibiotics and the cyclic polyether complexes. Electrodes based on antibiotics were first developed by Stefanac and Simon (119, 120), who studied nonactin, monactin and valinomycin and other antibiotics. Pioda et al. (121), using a dilute solution of valinomycin in diphenyl ether, obtained a slope of 58.3 mV/decade for K⁺ with a selectivity constant of $2.5 \times 10^{-4}$ for interference by Na⁺. Frant and Ross (122) achieved selectivity for potassium of $10^4$ over sodium using valinomycin with a variety of aromatic solvents such as nitrobenzene and higher homologues, diphenylether, chlorobenzene or bromobenzene. The linear response of the electrode covered the range from 1M to below $10^{-6}$ M of K⁺. Lal and Christian (123) studied the factors affecting the selectivity and the response of Orion potassium selective electrodes based on valinomycin. They found the slope to be 52 mV over the range $10^{-7}$ to $10^{-4}$ M of potassium. It has been reported that valinomycin solutions are not very stable and the response deteriorates with the solution also turning brown (124). Beckman Workers (125) used nonactin, monactin trinactin, valinomycin and enniatin B with mineral oil and compound lipid for constructing the solid state electrode.
The aromatic compound provides long term stability of the barrier and the compound lipid serves as solidification agent. An electrode for potassium employed a barrier material comprising a mixture of Nujol, diphenylether, lecithin, and valinomycin in a weight ratio of approximately 1:1:6:0.04. The electrode responded to potassium over the range 1 M to $10^{-5}$ M with slope of 59.16 mV. Valinomycin has been incorporated successfully in both PVC and silicone rubber membranes. The valinomycin based silicone rubber showed a 59 mV slope over the range $10^{-1}$ to $10^{-6}$ M of potassium. Less than 5% of valinomycin was enough for the preparation of good silicone rubber membrane electrode. The PVC membrane electrode did not work at all without the addition of a softener, dibutyl-phthalate. Fiedler and Ruzicka used the PVC valinomycin membrane in contact with a teflon graphite surface as mentioned previously. A good result was obtained by coating the valinomycin PVC on platinum wire provided that the coating was not more than 0.15 mm thick. A thicker coating gave sub-Nernstian response. Interference with K$^+$ valinomycin membrane electrode by certain surfactant compounds was reported and studied.

An electrode selective to NH$_4^+$ was prepared using nonactin as active material in silicone rubber by Guilbault and Nagy. The electrode was used as a urea electrode by covering the active surface with an immobilized urease enzyme layer. The electrode had good stability and response range. Also, nonactin was used by Beckman workers to prepare a solid state ammonium electrode.

Electrodes based on the cyclic polyether complexes,
crown compounds, appear not to have such good selectivity for $K^+$ over $Na^+$ as the antibiotic valinomycin being worse by a factor of a hundred. They can be usefully applied in practice in certain cases, however, because of their good properties (131). The basic structural feature of the crown compounds is the size of the macrocyclic ring and the number of oxygen atoms. Petranek and Ryba (132) studied PVC membrane electrodes for potassium based on 4-methylbenzo-15-Crown-5, dicyclohexyl 19-Crown-6, dibenzo 22-Crown-5, ditert-butyl-dibenzo-30-Crown-10, dinitrodibenzo-30-Crown-11 and dibenzo-36-Crown-12. They concluded that the selectivity constant indicated that the highest $K/Na$ selectivity is obtained in the group of crown compounds with eighteen-membered or nineteen-membered rings containing six oxygen atoms each and for thirty-membered rings with ten oxygen atoms. Poor $K/Na$ selectivity was displayed by 4-methylbenzo-15-Crown-5; with dibenzo-16-Crown-5 there was practically no difference between the response to potassium and sodium. Obviously, in both cases, the ring sizes and the number of binding sites represented by the oxygen atoms do not permit formation of a cavity suitable for complex formation with $K^+$. The 30-Crown-10 compounds were characterized by high flexibility of the macrocyclic ring which enables the compounds to complex the given cation by wrapping around it with a change in conformation similar to valinomycin. Substitution of dibenzo-30-Crown-10 with methyl or tert-butyl group not only affected the speed of the electrode response favourably but also the $K/Na$ selectivity which increased more than three fold and the electrodes had long useful lifetimes. Rechnitz and Eyal (133) studied some of the crown compound liquid state electrodes. They concluded that it is possible to predict selectivity properties from complex formation data between
the crown compound and the ion to be measured. They proposed the following approximation

\[ K_{\text{sel}}^{1,2} \approx \frac{K_{f,1}}{K_{f,2}} \]

where \( K_{\text{sel}}^{1,2} \) is potentiometric selectivity coefficient for the electrode response to ion 1 over 2 while \( K_{f,1} \) and \( K_{f,2} \) are the equilibrium formation constants for complexes between the carrier entity and ion 1 and 2 respectively. Some of the crown compounds were used by Beckman workers \((125)\) to prepare the solid state electrodes for potassium and ammonium ions. Morf, Kahr and Simon \((134)\) reported making an improvement in the performance of electrodes based on neutral carriers by incorporating lipophilic anions, such as tetraphenylborate, into the membrane. This reduced the anion interference in liquid membrane electrodes responsive to cations.

A barium ion selective electrode based on a neutral carrier complex was described by Levins \((135)\). The neutral carrier was a complex of a polyethylene glycol derivative which contains 12 ethylene oxide units per molecule of \( \text{Ba}^{2+} \) and 2 molecules of tetraphenylborate ion (12 EDU.ba.2TPB). The electrode is 10,000 times more selective to \( \text{Ba}^{2+} \) over \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) with Nernstian response over the range \( 10^{-1} \) to \( 10^{-5} \) M of barium ion.

A liquid state calcium selective electrode based on neutral carrier was described by Simon and More \((136)\). The structure of the ligand is shown below:
The selectivity constant for Ca²⁺ over Mg²⁺ was 3 x 10⁻⁵ which is the main advantage of using the neutral carrier calcium selective electrode.

Pungor et al (137) described an Fe³⁺ selective electrode based on hemine incorporated in silicone rubber. The hemine was prepared from blood. Further studies showed that the liquid membrane electrode yielded better results (138). The selection of solvent was limited by the slight solubility of hemine. Nitrobenzene was found to be suitable. The electrode had Nernstian response to iron(III) in the range of 10⁻¹ to 10⁻⁴ M and it showed good selectivity to iron(III) in the presence of cobalt(II) and copper(II). Besides the direct measurement of the iron activity, the electrode was employed for potentiometric precipitation and complexation titrations as sensors. An attempt to prepare a neutral carrier ion selective electrode of Al³⁺ was made using aluminium oxinate dissolved in chloroform (138). The response of the electrode to aluminium was very weak and it is
also sensitive to hydrogen ion. It could be used successfully for precipitation titrations only.

Baumann (139) described a liquid state membrane electrode selective to strontium based on a strontium polyethylene glycol complex as a neutral carrier. The electrode is selective to strontium in the presence of alkali ions, calcium and some other divalent ions. The selectivity decreases with decreasing strontium ion concentration.
BASIC DYE SALTS

Entuistle and Hayes (140) were among the first to make successful use of basic dye salts in electrode technology. The active material consists of a solution of the ion-association complex formed between the uranyltribenzoate anion and the basic dye, Methylene Blue, dissolved in o-dichlorobenzene. The membrane was supported directly on graphite or an inert membrane was interposed between the graphite and the measured aqueous solution. The electrode, according to them, is strictly ion-selective for the uranyltribenzoate anion. The response of the electrode was Nernstian above $2 \times 10^{-6}$ M. Earlier work in this laboratory successfully used Brilliant Green dye to prepare electrodes selective to tetrathiocyanatozincate(II) (141), perchlorate (142), and tetrafluoroborate (143). The tetrathiocyanatozincate electrode was used to determine zinc(II) in the presence of thiocyanate ion over the range $10^{-1}$ to $10^{-4}$ M of Zn$^{2+}$. The electrode did not respond to zinc or thiocyanate ion when one of them was present in the solution alone. No interference was observed from copper(II), lead, nickel and copper(I) but iron(III) and cobalt did interfere. From the active material, which was the ion association complex formed between the tetrathiocyanatozincate ion and Brilliant Green, liquid state, heterogeneous silicone rubber and carbon paste electrodes were prepared. The best performance was observed using the liquid state electrode. The perchlorate electrode, which was based on Brilliant Green perchlorate, responded to perchlorate over the range $10^{-1}$ to $10^{-4}$ M of perchlorate with no significant interference from bromide, acetate, chloride or fluoride but with a little interference from iodide, bicarbonate and nitrate.
The electrode was used in potentiometric titrations of perchlorate with tetraphenylarsonium chloride. The tetrafluoroborate electrode responded in the range of $10^{-1}$ to $10^{-4}$ M of $\text{BF}_4^-$ The only serious interference was the perchlorate ion. The liquid state electrode used in the work will be discussed in detail later.

The ion association complexes between Crystal Violet and malic or phthalic acids were the active materials for the liquid state electrodes selective to malic and phthalic acid respectively\(^{(96)}\). Ishibashi et al\(^{(144)}\) used Crystal Violet ion association complexes to prepare liquid state electrodes selective to vitamin B\(^1\), methacholine, p-aminosalicylic acid and neostigmine. Ishibashi et al\(^{(145)}\) also studied electrodes selective to aromatic sulphonates based on ion association complexes formed between Crystal Violet, Methyl Violet, Malachile Green or Fuchsine Basic and aromatic sulphonate. The Crystal Violet aromatic sulphonate pair, had good sensitivity showing an approximately Nernstian response down to $10^{-4}$ M of sulphonate.

The potential of the electrode was independent of pH variation from 2.5 to 12 and chloride and sulphate ions in the aqueous sample solution did not affect the electrode potential. 1,3,6-naphthalenetrisulphonate exerted essentially no influence on the potential of $\alpha$-naphthalenesulphonate electrode. The interference of nitrate was large. Electrodes selective to dodecylsulphate based on a number of large organic cations including Crystal Violet and dodecylsulphate anion in o-dichlorobenzene gave unstable and rapidly increasing potential values above about $4 \times 10^{-3}$ M sodium dodecylsulphate\(^{(145)}\). This was ascribed to solubilization of the complex by sodium dodecylsulphate solution immediately adjacent to the electrode sensing surface.
OTHER ORGANIC SALTS USED

Ruzicka and Tjell\(^{(147)}\) used dithizonate for preparation of liquid state metal cation selective electrodes. They described a theory which would allow them to predict electrode properties from extraction data. They concluded that the higher the extraction constant, the higher the selectivity, the higher the sensitivity, the more positive the potential and the smaller is the influence of hydrogen ions. They found also that the higher the concentration of the active material in the organic phase, the more negative is the potential. When low concentrations of the metal ion are to be measured the pH of the solution would be high in order to avoid the interference of hydrogen ions. The stability and reproducibility of electrodes for Cu\(^{2+}\), Hg\(^{2+}\), Ag\(^+\), Zn\(^{2+}\) and Pb\(^{2+}\) were studied. Through all their study they found that a thin layer of the organic phase absorbed on the surface of hydrophobized carbon functioned better than using the body of Orion liquid-liquid membrane electrode. Ruzicka et al\(^{(148)}\) summarised some of the compounds which can be used on the selectrode or as liquid type. The most interesting compound was copper(II) diethyldithiocarbonate which yielded copper(II) selectrode with Nernstian response down to ca. \(pCu 8\) at pH 8.

Electrodes selective to tetrabutylammonium and tetrahexylammonium ions were based on PVC membranes containing N,N-dimethyl oleamide, as plasticizer\(^{(149)}\). The electrode also responded to tetraphenylboron and was successfully applied in potentiometric titration of the drug cation, diphenylhydramine with sodium tetraphenylboron. Further work\(^{(150)}\) showed that the electrode can be
used to determine dextromethorphan hydrobromide by titrating it with sodium tetraborylboron. The same paper described an electrode, based on PVC membrane containing dioctylphthalate plasticizer, responsive to $\text{Bu}_4\text{N}^+$, $\text{Pr}_4\text{N}^+$, tetrapentylammonium ion and tetrahexylammonium ion. Observation was made (149) that the response of the electrode to tetrahexylammonium ion appears to be consistently 350 mV greater than that to tetrapropylammonium ion. This greater effect was qualitatively in agreement with the free-energy requirement for transfer of twelve-CH$_2$-groupings from a lipoidal to an aqueous environment.

Tetraphenylanerounium thiocyanate was the basis of the SCN-liquid state ion selective electrode (151). The electrode responded to other anions with decreasing selectivity in the following order: 
$\text{ClO}_4^- > \text{I}_4^- > \text{SCN}^- > \text{I}^- > \text{ClO}_3^- > \text{NO}_3^- > \text{Br}^- > \text{BrO}_3^- > \text{Cl}^-$. 
A vitamin liquid state electrode was based on pyridoxine dipicrylamine (118). The electrode had Nernstian response to pyridoxine over the range $10^{-1}$ to $10^{-5}$ M. An electrode based on liquid anion exchanger tridecylamine hydrochloride was specific to bicarbonate in the presence excess $\text{AcO}^-$, $\text{SO}_4^{2-}$ and $\text{HPO}_4^{2-}$ (152). The active material for a selenium liquid state electrode was 3,3-diaminobenzidine in hexane (153). The electrode showed a fairly good selectivity to Se over other ions but was not useful below $10^{-4}$ M of Se. Electrodes, based on bis(0,0'-diisobutyl-dithio-phosphato)nickel(II), cadmium(II) or lead(II) in chlorobenzene, responded very selectively to Ni$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$, respectively, over the range $10^{-1}$ to $10^{-4}$ in the presence of alkali and alkali earth metals (154). Gvanch and Bertrand (155) used dodecylsulphate($\text{OS}^-$), tetrapropylbenzenesulphate($\text{TPBS}^-$) and dioctylsulphosuccinate($\text{DOSS}^-$) complexes of hexadecyldipyridinium as active
material to prepare a liquid state electrode for measuring the activity of DS\(^{-}\), TPBS\(^{-}\) and DOSS\(^{-}\) activity and for potentiometric titration of anionic detergent in aqueous solution. Skobets et al.\(^{(156)}\) described dropping nitrate selective electrodes based on tetraalkylphosphonium nitrate. The electrodes differ from membrane electrodes by simple construction and low internal resistance. The potential of such electrodes stabilised instantly and were stable with time owing to continuous regeneration of the surface of the organic phase. The electrodes had Nernstian response over the range 10\(^{-1}\) to 10\(^{-5}\) M of NO\(_3\)\(^{-}\) and the selectivity of the electrodes decreased in the order of tetracetyl > tetraoctyl > tetraamylphosphonium nitrate. Sharp\(^{(157)}\) recently examined some organometallic substances for ion selective electrodes. Electrodes for Cu\(^{2+}\) based on copper tetracyanoethylene had Nernstian responses over the range 10\(^{-1}\) to 10\(^{-5}\) M of copper(II). Electrodes for sulphate, based on (Ph\(_3\)Pb)\(_2\)SO\(_4\) in o-dichlorobenzene, had linear response over the range 10\(^{-1}\) to 10\(^{-5}\) M of SO\(_4\)\(^{2-}\) but a slope of 22 mV per decade only. Some other compounds were examined but Nernstian response was not observed.
Suppose we have two solutions containing ions i and j separated by an ion selective membrane which allows ion i to move freely across the membrane from the solution of higher activity, \( a_i^1 \), to the solution of lower activity, \( a_i^2 \), and prevents ion j from passing through the membrane. In the membrane between the two solutions, a potential difference, i.e., the membrane potential, will arise:

\[
\mathcal{E}_m = \frac{2.303 \cdot R \cdot T}{Z_i \cdot F} \log \frac{a_i^1}{a_i^2} \quad \ldots \quad (1)
\]

This equation is equivalent to the Nernst equation for a concentration cell, where:

- \( R \) = the Gas Constant (8.3143 J K\(^{-1}\) Mol\(^{-1}\));
- \( T \) = the absolute temperature;
- \( F \) = the Faraday Constant (96487 C Mol\(^{-1}\)); and
- \( Z \) = the charge on ion i.

If the activity \( a_i^2 \) on one side of the membrane is kept constant, equation (1) can be converted into the form

\[
\mathcal{E}_m = \text{const.} + \frac{2.303 \cdot R \cdot T}{Z_i \cdot F} \log a_i^1 \quad \ldots \quad (2)
\]

Such a potential cannot be measured directly but can be deduced from the emf of an electrochemical cell.

\[
E = E^0 + \frac{RT}{ZF} \log a_i \quad \text{cation} \quad \ldots \quad (3)
\]
\[
E = E^0 - 2.303 \frac{RT}{ZF} \log a_i \quad \text{anion} \quad \ldots \quad \ldots \tag{4}
\]

\(E^0\) is a constant potential, the value of which depends on the choice of reference electrodes.

If the same reference electrode is used throughout, the value of \(E^0\) remains fixed. The term \(2.303 \frac{RT}{F}\) has a fixed value at a given temperature (59.16 mV at 25°C). Therefore, the value of potential \(E\) depends only on \(\log a_i\). In practice, no membrane electrode is specific for a particular ion; therefore, within certain limits, other ions in the solution contribute to the membrane potential. In such cases, the Nernst equation will be modified as

\[
E = E^0 + 2.303 \frac{RT}{ZF} \log \left( \frac{a_i}{a_i + K_{ij}(a_j)^{z/y}} \right) \quad \ldots \quad \ldots \tag{5}
\]

where \(K_{ij}\) is the selectivity constant of the interfering ion \(j\) relative to primary ion \(i\) for the given electrode. \(z\) and \(y\) are the charge on ions \(i\) and \(j\) respectively. A knowledge of the value of \(K_{ij}\) is of great importance when ion selective electrodes are being used in mixed solutions because it provides an indication of the concentration of an interfering ion that can be tolerated relative to the concentration of the primary ion. For all values of \(K_{ij} < 1\), the better the electrode is at least with respect to selectivity favouring the ion \(i\). Care should be taken in using the term 'selectivity constant' as it can be misleading in several ways. Firstly, the value for any two ions is activity dependent. Secondly, any quoted value depends on whether potentials are taken in mixed or separate solutions containing the two ions. An additional problem
with selectivity constants is that they are occasionally given as reciprocals \((K_{ji})\) or listed simply as \(K\). The various methods for evaluating selectivities, based on potential measurements in separate and mixed solutions were discussed by Moody and Thomas\((50)\).

Eisenman\((158)\) showed that, for solid state electrodes, the selectivity constant was determined by the product of the mobility ratio \((U_j/U_i)\) and the equilibrium constant \((K_{ij})\) of the ions \(i\) and \(j\). The two factors tend to oppose one another. It is also possible to predict the order of the selectivity from the solubility products. For example, \(I^- > Br^- > Cl^-\) is the order for the silver halides.

For liquid state electrodes, when there is negligible association in the organic phase, the selectivity constant depends on the product of the partition coefficient ratio of the dissociated ion species \((K_j/K_i)\) and the ratio of the summed mobilities of the dissociated ions and the dissociated sites \((U_j + U_s)/(U_i + U_s)\). This indicates that the solvent has a very important role in determining the selectivity constant. When there is strong association in the organic phase, the selectivity will depend on the product of the mobility ratio of the neutral pairs \((U_{js}/U_{is})\) and the ion exchange equilibrium constant \((K_{ij})\).
BASIS OF THE PRESENT WORK

Current interest in research in developing new ion-selective electrodes for a variety of ions lies mainly in their useful application in potentiometric analysis which is comparatively simple, inexpensive and readily automated.

The present work on ion-selective electrodes was undertaken in order to study some basic dye complexes as active materials for ion-selective electrodes. The work had its origins in this laboratory in two ways. Firstly, extensive use of basic dyes for colorimetric analytical determinations of a number of elements had been made here (159-163). Secondly, successful applications of Brilliant Green complexes in developing electrodes selective to tetrathiocyanatozincate(II), perchlorate and tetrafluoroborate (141-143) had been made.

Most of the present effort was directed to the development of new ion-selective electrode for SbCl$_6$\(^-\), TlCl$_4$\(^-\), SbCl$_4$\(^-\), AuCl$_4$\(^-\), HgBr$_3$\(^-\) and dodecylsulphate. Attempts were also made to develop electrodes selective to InBr$_4$\(^-\), FeCl$_4$\(^-\), azo dye anions, basic dye cations and some other ions.

Certain other organic compounds have been studied as potential active materials for ion-selective electrodes.
THE USE OF THE BASIC DYE REAGENTS

The importance of the basic dyes is already well known in the field of colorimetry. These dyes have been widely used for analytical determinations of numerous elements and these methods have been reviewed (164-166) in some detail. Two main groups of dyes have been used; xanthene dyes and triphenylmethane, but some use has been made of azine, oxazine, thiazine and other dyes. Many xanthene dyes can be used in fluorimetric work as the oxygen bridge of the xanthene cation causes it to be more rigid. Extraction blanks with these dyes tend to be higher than with the triphenylmethane dyes.

The basic dyes are sensitive reagents for the extractive photometric determination of those anions which form suitable ion-association complexes. The anion extracted may be a simple oxyanion, such as ClO₄⁻ or ReO₄⁻, or it may be a halo- or thiocyanato- complex anion, such as TlBr₄⁻, SbCl₆⁻ or Zn(SCN)₄²⁻. Some selectivity can be attained by the choice of medium in addition to the choice of dye. Further selectivity is obtained due to the fact that many elements react in only one oxidation state. Thus, antimony and thallium have to be oxidized to the +V and +III state respectively, and tin has to be reduced to Sn(II). In general, an increase in molecular weight of the dye cation increases the solubility of the ion pair in the organic solvent but decreases its selectivity. The dyes have the advantage of being intensely coloured with molar absorptivities of between 60,000 and 120,000 (1 mole⁻¹ cm⁻¹).

The selective formation of basic dye association complexes
with particular anions and their rapid complete extraction in hydrophobic solvents gives an indication of great potential for their use.

Some examples of successful applications of basic dye salts as active materials for ion-selective electrodes have been mentioned earlier.
ION-SELECTIVE ELECTRODES FOR THE DETERMINATION OF
ANTIMONY AND THALLIUM

INTRODUCTION

Basic dye extraction procedures have been developed in this laboratory for the determination of antimony and thallium (161-163). In these procedures, antimony and thallium were extracted into toluene from 2M hydrochloric acid solution as the hexachloroantimonate(V) and tetrachlorothallate(III) salts of Brilliant Green. Fogg et al. (161-163) discussed the problems associated with the colorimetric determination of antimony with Brilliant Green which include ensuring complete oxidation of antimony(III) to antimony(V), preventing hydrolysis of hexachloroantimonate(V), the necessity to use a pure sample of Brilliant Green, and the further protonation of the Brilliant Green cation at high acidities. The additional aminc groups in Brilliant Green and most common basic dye cations are protonated in 2M hydrochloric acid solution giving unextractable multivalent cations. The rate of this protonation is sufficiently slow that the extraction of antimony is possible provided the extraction is made immediately on addition of the Brilliant Green to the acidified solution. However, Brilliant Green hexachloroantimonate is unsuitable for application in ion selective electrodes owing to this further protonation.

Several basic dyes, Sevron Red L (C I Basic Red 17), Sevron Red GL (C I 11,085), Flavinduline O (C I 50,000) and Phenazinduline O, which are less readily protonated in 2M hydrochloric acid solution were studied in this laboratory with a view of using them as colorimetric reagents. These dyes were not entirely satisfactory for that
purpose for reasons of low extractability or low molar absorptivity.

The main object of the present work was the preparation of the hexachloroantimonate(V) and tetrachlorothallate(III) salts of these basic dyes and testing their suitabilities for use in liquid state ion-selective electrodes.

Samples of Sevron Red L and Sevron Red GL were obtained from the manufacturers (du Pont). The structure of Sevron Red GL is as shown below, but the structure of Sevron Red L has not been disclosed by the manufacturers.

![Structure of Sevron Red GL](image)

The other two dyes are not available commercially. Flavinduline O was prepared by the procedure given in the original patent\(^\text{(167)}\) and Phenazinduline O was prepared by the procedure given by Fogg et al\(^\text{(168,169)}\).

**EXPERIMENTAL**

**Preparation of Flavinduline O(III)**

4.2 g of 9,10-phenathaquinone(I) and 3.7 g of \(\text{o-aminodiphenylamine(II)}\) were dissolved in 75 ml of glacial acetic acid. The mixture was then boiled with 1500 ml of water containing 20 ml of concentrated hydrochloric acid and allowed to cool. The liquid was then filtered
and the dye precipitated as the zinc double chloride, hexachloroantimonate(V) or as tetrachlorothallate(III).

\[
\text{(I)} \quad \text{(II)} \quad \text{(III)}
\]

**Preparation of Phenazinduline O(V)**

1.05 g of 4,7-phenanthroline 5,6-dione (Phanquone - C.I.B.A.) (IV) was suspended in 60 ml of boiling ethanol and 0.9 g of o-aminodiphenylamine (II) in 10 ml of ethanol added. The mixture was refluxed for 2 hours on a water bath. The majority of the ethanol was distilled off under reduced pressure. 2 ml of 50% v/v hydrochloric acid and 50 ml of water were added and the solution boiled, cooled, and filtered. The dark brown coloured dye was then precipitated as the zinc double chloride or as the tetrachlorothallate(III) salt. The hexachloroantimonate(V) and tetrachloroantimonate(III) salts did not precipitate.
The Spectrum of the Dyes

The spectra of flavinduline O(V) in ethanol and concentrated hydrochloric acid were very similar, which indicates that the dye is not protonated further in the concentrated hydrochloric acid solution. The spectrum of Sevron Red L was similarly little changed on changing from water to 2M hydrochloric acid solution. Sevron Red GL, however, showed some change in its spectrum when the hydrochloric acid concentration exceeded 2M (168). The colour of an aqueous solution of phenazinduline O deepened increasingly as the concentration of hydrochloric acid was increased to 5M, although the spectrum was not changed markedly.

Preparation of Hexachloroantimonate(V) and Tetrachlorothallate(III) Salts of the Basic Dyes

Solutions containing hexachloroantimonate(V) and tetrachlorothallate(III) ions in 6M hydrochloric acid were prepared by oxidizing solutions of potassium antimony tartrate and thallium(I) sulphate.
with sodium nitrite. Excess nitrite was reduced with urea and the solutions were diluted to give a hydrochloric acid concentration of 2M before adding the solutions of aqueous solutions of the dyes. The addition was made slowly with continuous stirring of the dye solutions. The precipitated salts were allowed to stand for about one hour, filtered, washed with 2M hydrochloric acid solution and dried at room temperature or in an oven in which the temperature was not allowed to exceed 60°C. Cerium(IV), which is a superior oxidant to nitrite, could not be used in this work as both cerium(IV) and cerium(III) interfered in the potentiometric measurements made with the membrane electrode.

It was not found possible to obtain a precipitate of the hexachloroantimonate of Phenazinduline O using the above procedure.

The Electrode Assembly

The liquid-state electrode assembly used in these studies has been developed in this laboratory and has been described by Fogg et al. (141). The electrode was fabricated from P.T.F.E. tube (½" internal and 1½" external diameters). A ½" section was cut from the end of the tube and threads were cut into two parts so that they can be screwed together and hold a rubber membrane of ½" diameter. Electrical contact with the back of the membrane was made with an ½" diameter carbon rod which just fitted the tube and which was held firmly in place by a narrow nylon screw passing through the main body of the electrode. Connection with the pH-meter was made through a coaxial cable connected to the carbon rod by means of a conducting thermosetting silver resin preparation (Johnson Matthey Metal Limited). A
commercial natural rubber (Harborough Rubber Company) of 2.70 mm in thickness as well as a natural rubber, especially prepared for this purpose, in the Department of Polymer Technology, were used to prepare the membrane of the electrode. A \( \frac{1}{2} \)" disc rubber membrane was soaked in an organic solution of a basic dye salt till it became saturated and the dye salt was desirably evenly distributed in the rubber matrix. The rubber disc has about \( \frac{3}{4} \)" diameter after swelling in a number of organic solvents. The complete electrode is shown in Fig 1.

Preparation of the Membrane and the Use of the Electrode

Membranes used in the present studies were soaked in a saturated solution of the appropriate basic dye salt in o-dichlorobenzene overnight. The membrane was used in the above-mentioned electrode assembly. The resulting ion-selective electrode was used in an electrochemical cell which may be shown diagramatically as

| Ion-selective electrode | Sample Solution | Reference Electrode |

The temperature of the cell was maintained at \(-25^\circ C\) during the entire work, using a flow-through jacketed beaker, a small water pump and a thermostatically controlled water bath. This system controlled the temperature of the solution in the beaker within \( \pm 0.2^\circ C\). An electromagnetic stirrer was used for stirring purposes. The potential measurements were made with a Pye 290 pH meter versus a saturated calomel electrode.

Standard solutions of hexachloroantimonate(V) and tetrachloro-
Natural-rubber membrane liquid-state electrode
thallate(III) in 2M hydrochloric acid solution were prepared as indicated previously from potassium antimony tartrate and thallium(I) sulphate. Standard antimony(III) solutions were prepared similarly but omitting the oxidation step. Both hexachloroantimonate(V) and tetrachloroantimonate(III) standard solutions are not very stable and must be prepared before use from aqueous standard solutions of potassium antimony tartrate which are very stable(163).

RESULTS

Liquid state electrodes based on the hexachloroantimonate and tetrachlorothallate(III) salts of Sevron Red L, Sevron Red GL and Flavinduline O were tested and were found to behave in a Nernstian manner. Electrodes based on the zinc double chloride and tetrachlorothallate(III) salts of Phenazinduline O behaved similarly.

The electrodes were found to be interchangeably responsive to antimony(V), antimony(III), and thallium(III) in 2M hydrochloric acid. That is, the Sevron Red L hexachloroantimonate(V) electrode became responsive to the tetrachlorothallate(III) ion, for example, when it was soaked in a solution of the latter ion for 2 hours. As Phenazinduline O hexachloroantimonate(V) could not be precipitated directly, it was prepared in situ in the membrane by treating the zinc double chloride electrode with hexachloroantimonate(V). All the electrodes needed conditioning for two hours at least in $10^{-3}$ M solution of the ion to be measured.

The response of several of these electrodes is given in Tables
1 and 2, and shown in Fig 2.

It was seen that these electrodes responded to antimony(III) as well as to antimony(V), and it was confirmed that antimony(III) is extracted into o-dichlorobenzene from 2M hydrochloric acid solution by these basic dyes, albeit with a high blank, presumably as the tetrachloroantimonate(III). The response of the electrodes were Nernstian when hexachloroantimonate or tetrachlorothallate ions were tested but slightly less (57 - 50 mV) when tetrachloroantimonate was tested. The selectivity of all electrodes were in the order Sb(V) > Ti(III) > Sb(III).

The electrode potential drifts in one particular direction and the extent of the drift depends on the dye salt used and on the rubber. The drift is more marked after 1 day of preparation than for the following 4 weeks. For this reason, it is desirable to leave the electrode in contact with a 10⁻³ M solution of the ion to be determined overnight before use. In any event, on one particular day, the reproducibility is good, i.e. within 1 mV, when Sevron Red L and Phenazinduline O salt are used. The Flavinduline electrode showed an overall shift of 50 mV after one day of preparation, 74 mV after 10 days and 84 mV after 15 days, while Sevron Red L electrodes showed 2 mV shifts after 5 days and no further shift in the following 20 days. The Phenazinduline O electrode was as good as the Sevron Red L electrode but the Sevron Red G1 electrode showed a 4 mV shift after one day and 13 mV after 7 days. These figures were observed when lightly cross-linked natural rubber was used. The extent of the potential drifts was much higher when highly cross-linked natural rubber was used.
<table>
<thead>
<tr>
<th>Electrode Used</th>
<th>SbCl$_6^-$</th>
<th>TlCl$_4^-$</th>
<th>SbCl$_4^-$</th>
<th>SbCl$_6^-$</th>
<th>TlCl$_4^-$</th>
<th>SbCl$_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion Measured</td>
<td>Ion Conc.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10^{-2}$ M</td>
<td>-425.5</td>
<td>-296.5</td>
<td>-114.0</td>
<td>-387.5</td>
<td>-251.9</td>
<td>-85.5</td>
</tr>
<tr>
<td>$10^{-3}$ M</td>
<td>-364.4</td>
<td>-239.5</td>
<td>-57.1</td>
<td>-329.1</td>
<td>-189.1</td>
<td>+23.1</td>
</tr>
<tr>
<td>$10^{-4}$ M</td>
<td>-303.9</td>
<td>-187.0</td>
<td>-15.5</td>
<td>-273.2</td>
<td>-134.0</td>
<td>+61.3</td>
</tr>
<tr>
<td>$10^{-5}$ M</td>
<td>-244.0</td>
<td>-160.1</td>
<td></td>
<td>-204.1</td>
<td>-94.1</td>
<td></td>
</tr>
<tr>
<td>$10^{-6}$ M</td>
<td>-197.1</td>
<td></td>
<td></td>
<td>-146.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10^{-7}$ M</td>
<td>-152.2</td>
<td></td>
<td></td>
<td>-42.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10^{-8}$ M</td>
<td>-138.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10^{-9}$ M</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 1**  Potential response (mV) of electrodes based on Savron Red L hexachloroantimonate(V) and the Phenazindoline zinc double salt towards SbCl$_6^-$, TlCl$_4^-$ and SbCl$_4^-$.
<table>
<thead>
<tr>
<th>Ion Measured</th>
<th>( \text{SbCl}_6^- )</th>
<th>( \text{TlCl}_4^- )</th>
<th>( \text{SbCl}_4^- )</th>
<th>( \text{SbCl}_6^- )</th>
<th>( \text{TlCl}_4^- )</th>
<th>( \text{SbCl}_4^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^{-2} \text{ M} )</td>
<td>-257.5</td>
<td>+52.5</td>
<td></td>
<td>-316.2</td>
<td>-196.5</td>
<td>-42.5</td>
</tr>
<tr>
<td>( 10^{-3} \text{ M} )</td>
<td>-334.8</td>
<td>-198.0</td>
<td>+98.3</td>
<td>-256.3</td>
<td>-139.8</td>
<td>+7.0</td>
</tr>
<tr>
<td>( 10^{-4} \text{ M} )</td>
<td>-273.1</td>
<td>-139.6</td>
<td>+138.8</td>
<td>-170.5</td>
<td>-86.6</td>
<td>+58.1</td>
</tr>
<tr>
<td>( 10^{-5} \text{ M} )</td>
<td>-212.2</td>
<td>-91.5</td>
<td>+149.0</td>
<td>-107.4</td>
<td>-62.0</td>
<td>+93.3</td>
</tr>
<tr>
<td>( 10^{-6} \text{ M} )</td>
<td>-145.0</td>
<td>-81.9</td>
<td>+149.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 10^{-7} \text{ M} )</td>
<td>-65.2</td>
<td>-71.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 2** Potential response (mV) of electrodes based on Sevron Red GL hexachloroantimonate(V) and Flavinduline hexachloroantimonate towards \( \text{SbCl}_6^- \), \( \text{TlCl}_4^- \) and \( \text{SbCl}_4^- \).
**Fig 2**

ELECTRODE RESPONSE TO ANTIMONY(III) AND (V) AND THALLIUM(III)

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Ion</th>
<th>Electrode</th>
<th>Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Sevrol Red L</td>
<td>Sb(V)</td>
<td>(vii) Sevrol Red GL</td>
<td>Tl(III)</td>
</tr>
<tr>
<td>(ii) Phenazinduline*</td>
<td>Sb(V)</td>
<td>(viii) Flavinduline</td>
<td>Tl(III)</td>
</tr>
<tr>
<td>(iii) Sevrol Red GL</td>
<td>Sb(V)</td>
<td>(ix) Sevrol Red L</td>
<td>Sb(III)</td>
</tr>
<tr>
<td>(iv) Sevrol Red L</td>
<td>Tl(III)</td>
<td>(x) Phenazinduline*</td>
<td>Sb(III)</td>
</tr>
<tr>
<td>(v) Phenazinduline*</td>
<td>Tl(III)</td>
<td>(xi) Flavinduline</td>
<td>Sb(III)</td>
</tr>
<tr>
<td>(vi) Flavinduline</td>
<td>Sb(V)</td>
<td>(xii) Sevrol Red GL</td>
<td>Sb(III)</td>
</tr>
</tbody>
</table>

* The phenazinduline electrode was prepared from the zinc double salt: the electrodes of the other three dyes were prepared from the antimony(V) salt.
The electrodes gave steady responses within 3 minutes when they were moved from a more concentrated solution to a more dilute solution and less than 2 minutes for a move from the dilute solution to the more concentrated solution.

Study of Interfering Ions

Possible interference by certain ions was studied by observing the effect of $10^{-2}$ and $10^{-3}$ M concentrations of copper(II), mercury(II), lead and nickel, on the value of the potential obtained with the phenazinduline O hexachloroantimonate(V) electrode in contact with a $10^{-4}$ M antimony(V) in 2M hydrochloric solution. The change in the potential was very small (0 to -2 mV) indicating negligible interference by these ions.

As would be expected, interference was observed from zinc ion. When a Phenazinduline O hexachloroantimonate(V) electrode was placed in $10^{-3}$ M zinc solution in 2M hydrochloric acid, a steady response was observed only after two hours. After subsequent changes in the zinc concentration, steady responses were observed after 5 minutes. The potential versus pZn slopes were considerably less than Nernstian; 15, 10 and 5 mV per decade in the pZn range 2 to 3, 3 to 4 and 4 to 5 respectively. An electrode prepared from the Phenazinduline O zinc double salt and not previously treated with antimony(V) behaved similarly.
DISCUSSION

The electrodes described are suitable for determining antimony or thallium over a wide range of concentrations. The appropriate basic dye salts are readily prepared and it is convenient to store sufficient for all subsequent use. The membranes themselves are very readily prepared from these salts. Although a 2 hour swelling of the rubber in a saturated solution of the appropriate basic dye salt was sufficient when a lightly cross-linked natural rubber was used, a longer time was needed for the highly cross-linked natural rubber to swell. For this reason and because the potential drift was not as bad when the lightly cross-linked rubber was used, this rubber is recommended for general use. It was also noticed that in the case of the highly cross-linked natural rubber, the basic dye salt was not distributed uniformly throughout the rubber. There were clear signs of adsorption of the dye salt on the surface of the rubber which detracted from the reproducibility of the electrode response. It is recommended also to leave the rubber overnight in o-dichlorobenzene solution of the basic dye salt to ensure complete swelling and uniform distribution of the dye salt.

If the electrodes are stored in the o-dichlorobenzene solution of the basic dye salt, two hours conditioning in a $10^{-3}$ M solution of the relevant ion in 2M hydrochloric acid solution is required. For general use it is recommended that the electrode is stored in contact with a $10^{-3}$ M solution of the relevant ion in 2M hydrochloric acid solution. Storage in 2M hydrochloric acid solution, or, particularly, in water, in the absence of a responsive anion, is detrimental to the
condition of the electrode. Full response was obtained within $\frac{1}{2}$ hour after storing the electrode for one day in water, but storing it for longer periods resulted in an electrode which had a short lifetime and a less than full Nernstian response. The reproducibility of electrode response on any particular day is within $\pm 1$ mV. It was shown before how the potential response drifts from day to day and how electrodes made from Sevron Red L and Phenazinduline 0 have the smallest drifts. These electrodes were used satisfactorily for more than four weeks, whereas full response of the Flavinduline 0 and Sevron Red GL was lost after about ten days and twenty days respectively.

For general use, Sevron Red L and Phenazinduline 0 salts are recommended. In the case of Sevron Red L, the appropriate antimony or thallium salt should be prepared and used. In the case of Phenazinduline 0, although the thallium salt was tested, better results were obtained with the electrode prepared from the zinc double salt which was conditioned subsequently in an antimony(V) or thallium(III) solution.

The active material, Sevron Red L hexachloroantimonate, was found not to be suitable for use on a electrode or in preparing silicone rubber membranes. In the case of a electrode, the response was considerably less than Nernstian and was not reproducible while, in the case of silicone-rubber membranes, the membrane itself was very fragile. The mechanical properties of the membranes were not improved by changing the ratio of the active material in the matrix from 50% to 40% and 30%.
ION-SELECTIVE ELECTRODE FOR THE DETERMINATION OF GOLD

INTRODUCTION

A spectrophotometric method for determining gold with Brilliant Green was described by Fogg et al. The problems of the Brilliant Green protonation at higher concentration of hydrochloric acid have been mentioned previously. Although the extraction procedure is satisfactory if the extraction is made immediately on addition of Brilliant Green to the acidified gold solution, the Brilliant Green tetrachloroaurate is unsuitable for application in ion-selective electrodes.

Safranine O (Basic red 2 : C.I. 50240) is less readily protonated if the hydrochloric acid concentration is not too high. The analytically useful, R⁺ dye cation, is virtually non-existent at hydrochloric acid concentrations higher than 6M. The structure of the dye is shown below.

As the tetrachloroaurate anion does need a high concentration of hydrochloric acid in order to be formed (0.5 M hydrochloric acid),
the safranine 0 tetrachloroaurate was examined as an active material for liquid state ion-selective electrode for gold.

**EXPERIMENTAL**

**Preparation of Safranine 0 Tetrachloroaurate Salt**

The safranine 0 tetrachloroaurate(III) was prepared by precipitating the dye from acidic aqueous alcoholic solution 2:1 with gold solution in 0.5 M hydrochloric acid. The gold solution was added slowly associated with continuous stirring of the other solution. The precipitate was filtered off, washed with 0.5 M hydrochloric acid and dried at 70°C.

**Preparation of the Membrane and the Use of the Electrode**

As mentioned before, in the preparation of antimony and thallium electrodes, a \( \frac{1}{2} '' \) disc lightly cross-linked rubber membrane was soaked in a saturated solution of Safranine 0 tetrachloroaurate in o-dichlorobenzene overnight. The membrane, which was about \( \frac{3}{8} '' \) in diameter, was used in the electrode body described before. Potential measurements were made with a Pye 290 pH meter versus a saturated calomel electrode. The electrode was left overnight in contact with \( 2.5 \times 10^{-4} \) M gold in 0.5 M hydrochloric acid solution.

**RESULTS**

The prepared electrode was used to study its response to tetrachloroaurate anion and some interfering ions.
According to the Nernst equation, the potential of the electrochemical cell would be given as

$$E = E^0 - \frac{RT}{F} \log a_{\text{AuCl}_4^-}$$

This extent of response was obtained between $2.5 \times 10^{-4}$ and $2.5 \times 10^{-5}$ M of tetrachloroaurate but slightly less between $2.5 \times 10^{-5}$ and $2.5 \times 10^{-7}$. During the first 24 hours after the preparation of the electrode, the potential drifted by as much as 40 mV in the negative direction, whereas after 16 days, the potential was 32 mV more negative for the same concentration. The slope of the potential versus $p_{\text{AuCl}_4^-}$ remained the same. The reproducibility of the electrodes in a particular day, except during the first 24 hours after electrode preparation, was found within 1.0 mV. A steady response was obtained within 3 minutes when it was moved from a more concentrated solution to a more dilute one and less than 1.5 minutes for a move from the dilute solution to the more concentrated solution. Furthermore, at $2.5 \times 10^{-4}$ M and $2.5 \times 10^{-5}$ M, the potential was stable for about one hour, but a slight drift was noticed in negative direction when the electrode was used at lower concentration. The electrode was kept in $2.5 \times 10^{-4}$ M tetrachloroaurate solution when it was not in use.

The results obtained with the electrode are listed in Table 3 and shown graphically in Fig 3.

Table 4 shows the potential readings over a period of 16 days for $2.5 \times 10^{-4}$ M $\text{AuCl}_4^-$ solution and Fig 4 shows these results graphically.
### TABLE 3
Response of the electrode based on Safranine 0 tetrachloroauroate toward AuCl$_4^-$ on the day of the electrode preparation and after 16 days.

<table>
<thead>
<tr>
<th>AuCl$_4^-$ conc. (M)</th>
<th>pAuCl$_4^-$</th>
<th>Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>On Preparation Day</td>
<td>After 16 days</td>
</tr>
<tr>
<td>$2.5 \times 10^{-4}$</td>
<td>3.61</td>
<td>-219.5</td>
</tr>
<tr>
<td>$2.5 \times 10^{-5}$</td>
<td>4.61</td>
<td>-160.5</td>
</tr>
<tr>
<td>$2.5 \times 10^{-6}$</td>
<td>5.61</td>
<td>-104.0</td>
</tr>
<tr>
<td>$2.5 \times 10^{-7}$</td>
<td>6.61</td>
<td>- 50.1</td>
</tr>
</tbody>
</table>

### TABLE 4
Response of the Safranine 0 tetrachloroauroate electrode to $2.5 \times 10^{-4}$ M AuCl$_4^-$ over a period of 16 days.

<table>
<thead>
<tr>
<th>Age of the electrode</th>
<th>Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 hours</td>
<td>-219.0</td>
</tr>
<tr>
<td>1 day</td>
<td>-260.2</td>
</tr>
<tr>
<td>2 days</td>
<td>-263.1</td>
</tr>
<tr>
<td>6 days</td>
<td>-270.3</td>
</tr>
<tr>
<td>16 days</td>
<td>-291.0</td>
</tr>
</tbody>
</table>
Fig 3

Response of electrode based on Safranine O tetrachloroaurate to tetrachloroaurate anion.

(i) 16 days after electrode preparation

(ii) on the day of preparation
Fig 4

Response of Safranin O tetrachloroaurate electrode to $2.5 \times 10^{-4}$ M $\text{AuCl}_4^-$ over a period of 16 days.
Study of the Interfering Ions

Possible interference by certain ions was studied by observing the effect of $10^{-3}$ M concentrations of copper(II), mercury(II), lead, zinc, antimony(III) and nickel, and of $10^{-2}$ M sulphate, nitrate and bromide, on the value of the potential with $2.5 \times 10^{-5}$ M $\text{AuCl}_4^-$ solution. The change in potential was very small (0 - 1 mV) indicating negligible interference by these ions. A 2.5 mV change in the potential was noticed when $10^{-1}$ perchlorate ions was in $2.5 \times 10^{-5}$ M $\text{AuCl}_4^-$. When the electrode was placed in $10^{-2}$ M perchlorate solution, a steady response was observed only after 1 hour. After subsequent changes in perchlorate concentration steady responses were observed after 3 minutes. The potential versus $p\text{ClO}_4^-$ slope was near Nernstian. These results are listed in Table 5.

<table>
<thead>
<tr>
<th>$\text{ClO}_4^-$ concentration (M)</th>
<th>Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-1}$</td>
<td>- 47.2</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>+ 1.0</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>+ 50.8</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>+ 90.6</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>+136.2</td>
</tr>
</tbody>
</table>

**Table 5** Response of the Safranine O tetrachloroaurate electrode to perchlorate.
Calculation of Selectivity Constant in Separate Solutions of Tetrachloroaurate and Perchlorate Anions

Selectivity constant is calculated, according to one of the methods described by Moody and Thomas\(^{(20)}\), as follows:

According to the Nernstian equation, the potential response, \(E_1\), to the primary anion is

\[ E_1 = E^0 - \frac{RT}{F} \log a_{\text{AuCl}_4^-} \quad \cdots \quad (6) \]

The potential response, \(E\), to an anion mixture, \(\text{AuCl}_4^- - \text{ClO}_4^-\), is given by

\[ E = E^0 - \frac{RT}{F} \log \left( a_{\text{AuCl}_4^-} + K_{\text{AuCl}_4^-/\text{ClO}_4^-} a_{\text{ClO}_4^-} \right) \cdots (7) \]

The potential response, \(E_2\), to the \(\text{ClO}_4^-\) anion can be obtained from equation (7) by making \(a_{\text{AuCl}_4^-} = 0\):

\[ E_2 = E^0 - \frac{RT}{F} \log K_{\text{AuCl}_4^-/\text{ClO}_4^-} a_{\text{ClO}_4^-} \quad \cdots (8) \]

Subtracting equation (6) from equation (8) gives

\[ E_1 - E_2 = - \frac{RT}{F} \log a_{\text{AuCl}_4^-} \\
+ \frac{RT}{F} \log K_{\text{AuCl}_4^-/\text{ClO}_4^-} \\
+ 2.303 \frac{RT}{F} \log a_{\text{ClO}_4^-} \quad \cdots \quad (9) \]
When the primary and interfering activity are equal, then equation (9) simplifies to

\[
\frac{E_1 - E_2}{0.94} = 2.303 \frac{RT}{F} \log K_{\text{AuCl}_4^-/\text{ClO}_4^-} \quad \ldots \quad (10)
\]

or

\[
\frac{E_1 - E_2}{2.303 \frac{RT}{F}} = \log K_{\text{AuCl}_4^-/\text{ClO}_4^-} \quad \ldots \quad (11)
\]

According to the above equation, the \(K_{\text{AuCl}_4^-/\text{ClO}_4^-}\) was calculated at \(10^{-4}\) M concentration of both tetrachloroaurate and perchlorate and it was found to be \(9.8 \times 10^{-6}\).

**DISCUSSION**

The tetrachloroaurate ion-selective electrode described here is another example of a successful electrode based on water-insoluble basic dye salts as ion sensors.

The electrode gives almost Nernstian response over a wide range of tetrachloroaurate. Although the measured potential of the electrode in the particular solution drifted the slopes nevertheless remained Nernstian for more than two weeks. The electrode needed re-conditioning for more than one hour after being used for testing the response to perchlorate in the absence of tetrachloroaurate. Storing the electrode in \(2.5 \times 10^{-4}\) M tetrachloroaurate solution was necessary when the electrode was not in use.

The active material was not suitable to be used on electrode as the response was considerably less than Nernstian and was not
reproducible. No response to the change in tetrachloroaurate concentration was noticed after 4 days.

The active material was also unsuitable for use in dichlorobenzene in U-tube as sub-Nernstian response was observed and the steady reading was obtained only after 30 min. The result was not very reproducible and there were practical difficulties in changing the solution and washing the cell.
INTRODUCTION

Several basic dyes, namely, Brilliant Green (159), Rhodamine B (170), Methyl Violet (171) and Safranine T (172), have been used in extraction photometric procedures for the determination of perrhenate. The Brilliant Green perrhenate ion-association complex showed the highest molar absorptivity (more than \(9.8 \times 10^4 \text{ mole}^{-1} \text{ cm}^{-1}\)) and extractability. The problems associated with the determination of antimony using Brilliant Green do not exist in the perrhenate determination as the extraction of the perrhenate ion was made at pH 6, which is the optimum pH for the \(R^+\) form of Brilliant Green.

In the present work Brilliant Green has been used to develop a liquid state ion-selective electrode sensitive to perrhenate.

EXPERIMENTAL

Preparation of Brilliant Green Perrhenate in o-Dichlorobenzene

No attempt was made to precipitate the Brilliant Green using potassium perrhenate as the latter is an expensive chemical. Alternatively, the Brilliant Green perrhenate was extracted into o-dichlorobenzene immediately after the addition of the Brilliant Green to the aqueous solution. The o-dichlorobenzene solution of Brilliant Green perrhenate was satisfactorily used for one year.
Reagents

1. Brilliant Green Solution, 0.05 per cent w/v in water.

2. Buffer solution, pH 6 – dilute 500 ml of 0.1 M potassium dihydrogen phosphate solution and 56 ml of 0.1 M sodium hydroxide solution to 1 litre with water in a calibrated flask.

3. Standard rhenium solution, $10^{-2}$ M of potassium perrhenate in water.

Procedure

A 20 ml aliquot of $10^{-2}$ M potassium perrhenate solution was introduced into a 250 ml separating funnel, 20 ml of buffer solution was added followed by 20 ml of Brilliant Green solution. The Brilliant Green ion-association complex was extracted with two 25-ml portions of o-dichlorobenzene. The o-dichlorobenzene solution was filtered through a filter paper.

Preparation of the Membrane and the Use of the Electrode

The natural rubber membrane was saturated with a o-dichlorobenzene solution of the dye salt by standing it in the solution overnight. After this time, the basic dye salt was seen to be evenly distributed through the membrane and the membrane swelled to nearly twice its original volume and thickness. The membrane was used in the electrode body as described earlier. Potential measurements were made with a Radiometer PHM64 Research pH meter versus a saturated calomel electrode. Standard solutions of potassium perrhenate were prepared by diluting $10^{-2}$ M potassium perrhenate standard solution.
RESULTS

The electrode prepared was left overnight in $10^{-3}$ M potassium perrhenate for conditioning. The electrode responded in a nearly Nernstian manner to the perrhenate anion. The response of the electrode to Brilliant Green was observed as well as to nitrate, thiocyanate and perchlorate. These results are listed in Table 6 and are shown graphically in Fig 5.

The potential of the electrode at a particular concentration of perrhenate drifted by 4 mV after 24 days of electrode preparation, but the slope of the potential reading versus pReO$_4^-$ did not change. A steady response was obtained within 2 minutes when the electrode was moved from a more concentrated solution to a more dilute solution and about 1 minute for a move from dilute solution to a more concentrated solution. The reproducibility in one particular day was within 0.5 and 1.0 mV. The electrode was left in contact with $10^{-3}$ M perrhenate solution when it was not in use.

Study of the Interferences

Possible interference was studied by observing the effect of $10^{-2}$ M concentration of copper sulphate, indium sulphate, zinc sulphate, sodium sulphate, sodium nitrate, sodium thiocyanate and sodium perchlorate, on the value of the potential obtained with perrhenate electrode in contact with a $10^{-4}$ M perrhenate. The change in the potential was very small in the presence of the sulphate of copper, indium, zinc and sodium (0 - 1 mV) indicating negligible interference by these ions. The change in the potential in the presence
<table>
<thead>
<tr>
<th>Ion to be tested</th>
<th>(\text{ReO}_4^-) with buffer</th>
<th>(\text{ReO}_4^-) without buffer</th>
<th>(\text{ClO}_4^-)</th>
<th>(\text{SCN}^-)</th>
<th>(\text{NO}_3^-)</th>
<th>Brilliant Green</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. (M)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10^{-1}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10^{-2}</td>
<td>+ 99.8</td>
<td>+ 93.4</td>
<td>+119.2</td>
<td>+156.5</td>
<td>+261.6</td>
<td>+379.4</td>
</tr>
<tr>
<td>10^{-3}</td>
<td>+153.2</td>
<td>+149.4</td>
<td>+174.7</td>
<td>+218.1</td>
<td>+289.1</td>
<td>+336.6</td>
</tr>
<tr>
<td>10^{-4}</td>
<td>+212.6</td>
<td>+206.1</td>
<td>+210.2</td>
<td>+268.8</td>
<td>+294.2</td>
<td>+305.8</td>
</tr>
<tr>
<td>10^{-5}</td>
<td>+261.1</td>
<td>+260.4</td>
<td>+255.1</td>
<td>+292.0</td>
<td></td>
<td>+300.0</td>
</tr>
<tr>
<td>10^{-6}</td>
<td>+273.7</td>
<td>+278.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 6**  Potential response (mV) of an electrode based on Brilliant Green perrhenate to \(\text{ReO}_4^-\), \(\text{ClO}_4^-\), \(\text{SCN}^-\), \(\text{NO}_3^-\) and the Brilliant Green cation.
Fig 5

RESPONSE OF THE BRILLIANT GREEN PERRHENATE ELECTRODE TO
$\text{ReO}_4^-$, $\text{ClO}_4^-$, SCN$^-$, NO$_3^-$ AND THE BRILLIANT GREEN CATION.

(i) $\text{ReO}_4^-$ (unbuffered)  
(ii) $\text{ClO}_4^-$  
(iii) SCN$^-$  
(iv) NO$_3^-$  
(v) Brilliant Green ($R^+$)
of perchlorate, thiocyanate and nitrate was 32, 26 and 3 mV respectively. The response of the electrode to the last three ions was then measured and the results are listed in Table 6.

The selectivity constant were calculated for $10^{-2}$ and $10^{-4}$ M solutions using the equation

$$\log K_{\text{ReO}_4^-/\text{interf. ion}} = \frac{E_1 - E_2}{2.303 \frac{RT}{Z_F}}$$

where $E_1$ and $E_2$ are the individual potentials measured in solutions of pure perrenate ion solution and interfering ion solution. The results are listed in Table 7.

<table>
<thead>
<tr>
<th>Interfering Ions</th>
<th>Selectivity Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^{-2}$ M</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>$8.33 \times 10^{-1}$</td>
</tr>
<tr>
<td>SCN$^-$</td>
<td>$6.99 \times 10^{-2}$</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>$4.3 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

TABLE 7 Selectivity Constant ($K_{\text{ReO}_4^-/\text{interf. ions}}$).

Study of pH Effects on Electrode Potential

The electrode was used to observe the effects of pH variations on the performance of the electrode. The results are listed in Table 8 and shown in Fig 6.
TABLE 8  Response of the electrode to pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>Potential (mV)</th>
<th>pH</th>
<th>Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.98</td>
<td>+210.4</td>
<td>7.18</td>
<td>+313.7</td>
</tr>
<tr>
<td>9.98</td>
<td>+233.6</td>
<td>5.96</td>
<td>+313.0</td>
</tr>
<tr>
<td>9.14</td>
<td>+278.8</td>
<td>5.01</td>
<td>+313.2</td>
</tr>
<tr>
<td>8.62</td>
<td>+293.0</td>
<td>3.99</td>
<td>+322.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.02</td>
<td>+393.0</td>
</tr>
</tbody>
</table>

DISCUSSION

The perrhenate ion selective electrode based on the Brilliant Green complex responded in a Nernstian or nearly Nernstian manner to perrhenate at pH 6. Slight improvement was noticed when a pure solution of potassium perrhenate was used but buffering the solution is to be recommended as the electrode response was affected by hydrogen ion concentration at high and low pH values. The electrode responded independently of pH between pH 5.01 and 7.18. The response time of the electrode was under 2 minutes and the potential drift was very small after 24 days (4 mV).

The electrode suffered from perchlorate and thiocyanate and to some extent nitrate interferences. The common cations, namely, Cu$^{2+}$, Zn$^{2+}$, Na$^+$ and K$^+$, do not interfere.
Thus the perrhenate liquid state electrode could be useful in direct determination of perrhenate in the absence of the interfering ions, as the electrode was used satisfactorily for about four weeks and the o-dichlorobenzene solution of Brilliant Green perrhenate was used to prepare an electrode after one year of preparation.
MERCURY(II) ION-SELECTIVE ELECTRODE

INTRODUCTION

A ceramic ion-selective electrode responsive to mercury(II) was developed by Liteanu et al. The electrode is more selective to silver ion.

The object of the present work was to investigate the behaviour of electrodes prepared from the tribromomercuric(II) salt of Methyl Green and from the mercury(II) complex of bithionol.

Methyl Green (C.I.42590) is a basic dye, having the triphenylmethane structure and containing three methylated amino groups, but one of them is trimethylated, so blocking resonance. It has been used principally by Lebedeva et al. for the colorimetric determination of mercury(II) by extraction of the dye-metal halide complex into benzene.

Bithionol precipitates mercury(II) in partly ethanolic medium but no precipitate is formed when bithionol is added to a solution of mercury(II) under similar conditions. It has been investigated earlier in this laboratory for use for a gravimetric procedure of mercury(II) by Gray.
EXPERIMENTAL

Preparation of Methyl Green Tribromomercurate(II) in o-dichlorobenzene

A solution $10^{-2}$ M in mercuric chloride and $10^{-1}$ M in potassium bromide was adjusted to pH 2 by the addition of sulphuric acid. A $10^{-2}$ M solution of Methyl Green was introduced to form the Methyl Green tribromomercurate(II) complex. This complex was extracted into dichlorobenzene.

Preparation of the Mercury(II) Bithionol Complex

The precipitate was prepared according to the method described by Gray (177). A solution $4 \times 10^{-3}$ M in bithionol and $5 \times 10^{-2}$ M in sodium acetate-acetic acid buffer in 1:1 v/v ethanol-water was used to precipitate mercury(II) from a solution containing $10^{-2}$ M mercury(II). The precipitate was filtered on a number four porosity sintered glass crucible, washed with water and with ethanol and dried at 50°C.

Preparation of the Membrane and the Use of the Electrode

The membranes for the liquid-state electrode were prepared as mentioned before, by soaking ½" discs of natural rubber in the dichlorobenzene solution of Methyl Green tribromomercurate or a saturated solution of bithionol mercury(II) complex in dichlorobenzene or in a 1:1 mixture of dichlorobenzene:nitrobenzene. The membranes swell to nearly twice the original size and thickness after leaving them overnight in the organic solution. Membranes did not swell at all in a nitrobenzene solution of the organic salt. The membranes were fixed in the electrode body as described before. Potential measurements were made with a Pye 290 pH meter versus a saturated calomel
electrode at 25°C.

RESULTS

The Methyl Green tribromomercurate electrode responded to $\text{HgBr}_3^-$ in an almost Nernstian manner in the range of $10^{-2}$ to $10^{-4}$ M $\text{Hg}^{2+}$ in $10^{-1}$ M potassium bromide. A steady potential response was obtained within 1 minute when the $\text{Hg}^{2+}$ concentration was more than $10^{-4}$ M, and after slightly longer periods of time at lower concentrations. The electrode potential drifted 17 mV after the first day of preparation and a further drift of 13.2 mV was recorded after 7 days of preparation. The slope of the potential versus pHgBr$_3^-$ remained unchanged after two weeks. The response of the electrode to HgBr$_3^-$ in the range $10^{-2}$ to $10^{-6}$ M is listed in Table 9 and shown graphically in Fig 7.

The mercury bithionol electrode, prepared in a mixture of dichlorobenzene and nitrobenzene (in a 1:1 ratio) responded in a near Nernstian manner to $\text{Hg}^{2+}$ in the range of $10^{-2}$ to $10^{-5}$ M. The electrode needed to be conditioned in $10^{-2}$ M $\text{Hg}^{2+}$ overnight. A steady response was obtained within 3 minutes in the range of $10^{-2}$ to $10^{-4}$ M $\text{Hg}^{2+}$, but the reading was not steady at $10^{-5}$ M $\text{Hg}^{2+}$ and the electrode did not give reproducible results after being in $10^{-5}$ M $\text{Hg}^{2+}$ solution.

The mercury bithionol electrode, prepared from solution of mercury bithionol in 100% dichlorobenzene, gave a less than Nernstian response in the range of $10^{-2}$ to $10^{-4}$ M $\text{Hg}^{2+}$ solution. and no
steady response was obtained at $10^{-5} \text{ M } \text{Hg}^{2+}$ solution. The electrode did not function at all after four days of preparation. The results obtained with the two electrodes are listed in Table 10 and shown graphically in Fig 7.

<table>
<thead>
<tr>
<th>HgBr$_3^-$ concentration (M)</th>
<th>Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-2}$</td>
<td>-16.0</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>+42.0</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>+97.9</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>+134.5</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>+150.1</td>
</tr>
</tbody>
</table>

**TABLE 9** Response of the Methyl Green tribromomercurate(II) electrode to HgBr$_3^-$.  

<table>
<thead>
<tr>
<th>Hg$^{2+}$ conc. (M)</th>
<th>Potential (mV)</th>
<th>Mercury bithionol in 1:1 dichlorobenzene and nitrobenzene electrode</th>
<th>Mercury bithionol in 100% dichlorobenzene electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-2}$</td>
<td>-66.7</td>
<td>-105.1</td>
<td></td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>-98.8</td>
<td>-133.2</td>
<td></td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>-130.0</td>
<td>-155.2</td>
<td></td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>-160.0 (not stable)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 10** Response of the mercury bithionol electrode to Hg$^{2+}$.  

ELECTRODE RESPONSE TO MERCURY

Electrode  

(i) Bithional mercury(II) in 100% o-dichlorobenzene  
(ii) Bithional mercury(II) in 1:1 o-dichlorobenzene : nitrobenzene  
(iii) Methyl Green tribromomercuric(II) in 100% o-dichlorobenzene  
(iv) Methyl Green tribromomercurate in 100% o-dichlorobenzene

Ion  

Hg\(^{2+}\)  
Hg\(^{2+}\)  
HgBr\(^{-}\)  
Br\(^{-}\) (in the presence of 10^{-4} N Hg\(^{2+}\))
Studying the Interference

The original paper determining mercury(II) using Methyl Green described interference by Au, Tl, Sb, Pb and Cd with the extraction of the dye-metal halide complex. These elements do not seem to interfere seriously with the functioning of the mercury(II) electrode based on Methyl Green HgBr$_3$. Also Zn(II), Co(II), Al(III), Ni(II) do not seem to interfere seriously, as well as Cl$^-$, PO$_4^{3-}$ and NO$_3^-$. This conclusion is made after observing the effect of $10^{-2}$ M concentration of these ions on the value of the potential obtained with the Methyl Green HgBr$_3$ electrode in contact with $10^{-3}$ M mercury(II) in $10^{-1}$ M potassium bromide. The change in potential was very small ($0 - 1.5$ mV). The same electrode suffered marked interference from Ag$^+$ and the electrode gradually converted to full response to Ag$^+$ when it was placed in $10^{-4}$ M silver ion in $10^{-1}$ M potassium bromide. At higher concentrations of silver ion, silver bromide is precipitated. The potential versus pH slope was less than Nernstian (about 50 mV) in the range of $10^{-4}$ to $10^{-5}$ M Ag in $10^{-1}$ M potassium bromide. The effect of hydrogen ion concentration was studied by observing the effect of pH change between pH 1 and 9 on a $10^{-3}$ M mercuric(II) in $10^{-1}$ M potassium bromide. There was no marked change in the potential reading between pH 2 to pH 8.

DISCUSSION

The mercury liquid state electrode based on Methyl Green HgBr$_3$ is suitable for determination of mercury(II) in $10^{-1}$ M KBr solutions over the range of $10^{-2}$ to $10^{-5}$ M Hg$^{2+}$. The dichlorobenzene solution of the dye salt is readily prepared and the membrane is also readily
prepared from this solution. It is recommended that the electrode be conditioned overnight in $10^{-3}$ M HgBr$_3$ solution as the potential drift was more marked after 24 hours of preparation than over the following 7 days. The slope of the potential reading versus pHgBr$_3$ remained unchanged after two weeks. The electrode must be operated with a bromide excess over mercury of at least ten fold. It is important to note that a bromide concentration greater than $10^{-1}$ M destroys the membrane. Similarly, contact with a concentrated mercury(II) solution before addition of the bromide causes stripping of bromide ion from the membrane complex. The exact concentration of the bromide ion is not critical as far as it is in a large excess as it is shown in the results in Fig 7, but it is recommended that it be kept at $10^{-1}$ M. The interference by silver ion is serious as the electrode is as selective to AgBr$_2$ as it is to HgBr$_3$. Silver ion also may cause other problems, namely stripping of the bromide ion from the membrane complex or precipitating the bromide if the silver is in high concentrations. Other ions do not interfere seriously.

The mercury(II) electrode based on bithionol mercury complex in o-dichlorobenzene is not suitable at all as the response is less than Nernstian, the range is limited and the electrode has a very short lifetime. An improvement in the electrode performance was made by using 1:1 dichlorobenzene-nitrobenzene. This may be due to the better solubility of the complex in nitrobenzene. Nitrobenzene alone cannot be used as the rubber does not swell in it at all. The reproducibility of the electrode is within 2mV in one particular day if it is used in solutions having concentrations between $10^{-2}$ to $10^{-4}$ M Hg$^{2+}$ but the performance of the electrode was not satisfactory after
using it to measure the response to $10^{-5}$ M Hg$^{2+}$.

The bithionol mercury complex was found not to be suitable for use as an active material on the selectrode or for preparing a Pungor-type silicone-rubber membrane.

In general, the bithionol mercury complex does not seem to be very promising as an active material to be used in ion-selective electrode while Methyl Green tribromomercurate(II) can be used satisfactorily to prepare liquid state electrode selective to HgBr$_3^-$.
INTRODUCTION

Surface active agents (surfactants) are either cationic, anionic, non-ionic or amphoteric surfactants. The anionic surfactants are the largest groups and are mostly either sulphated or sulphonated products while the cationic surfactants are mostly either quaternary ammonium or quaternary pyridine salts.

Considerable effort has been made to develop methods for effective determination of these compounds. The methods include those based on colorimetric titrations, gravimetric analysis and potentiometric procedures. Basic dyes have been used in spectrophotometric determinations of anionic surfactants.

Recently, ion-selective electrodes responsive to ionic surfactants have been developed by Birch and Clark, Fogg et al, and by Gavach et al.

The object of the present work was to prepare some basic dye salts of anionic surfactants and test their suitability for use in developing electrodes responsive to anionic surfactants. Methylene Blue and Methyl Green have been studied.

EXPERIMENTAL

Preparation of Methyl Green Lauryl Sulphate

Solutions containing Methyl Green (10^{-2} M), sodium lauryl
sulphate \((10^{-3} \text{ M})\) and a glycine hydrochloric acid buffer \((\text{pH 2.5})\) were prepared and combined according to Moore and Kolbeson \((183)\).

The glycine hydrochloric acid buffer was prepared by the dilution of solutions of glycine \((7.5 \text{ g})\) and sodium chloride \((5.8 \text{ g})\) to 1 litre and the addition of \(10^{-1} \text{ M}\) hydrochloric acid to produce a pH of 2.5.

Extraction is achieved by the use of 1:1 o-dichlorobenzene:nitrobenzene. A surfactant concentration in excess of \(10^{-3} \text{ M}\) prevented extraction of the complex by emulsion formation. Also the extraction was difficult using o-dichlorobenzene alone as emulsion was formed.

**Preparation of Methylene Blue Manoxol OT**

Solutions containing Methylene Blue \((10^{-2} \text{ M})\), Manoxol OT \((2 \times 10^{-3} \text{ M})\) and alkaline phosphate \((\text{pH 10})\) were prepared and combined according to the procedure of Longwell and Maniece \((180)\).

The extraction is achieved by the use of either 1:1 dichlorobenzene: nitrobenzene, for the preparation of the liquid-state electrode, or chloroform for preparing the solid material. This was done by evaporation of the chloroform under reduced pressure.

**Preparation of the Membrane and the Use of the Electrode**

The membranes for liquid-state electrodes were prepared, as mentioned before, by soaking the rubber membrane in the solution of the appropriate basic dye salt in 1:1 o-dichlorobenzene:nitrobenzene overnight. Potential measurements were made with a Yze 290 pH meter versus a saturated calomel electrode. Standard solutions of sodium lauryl sulphate \((C_{12}H_{25}O_5SNa)\) and Manoxol OT \((\text{sodium dioctyl sulphosuccinate}, C_{20}H_{37}NaO_7S)\) were prepared by dissolving the appropriate weight of the surfactant in water. Glycine hydrochloric acid buffer
was added to the standard solutions of lauryl sulphate and alkaline phosphate buffer to Manoxol OT standard solution.

**RESULTS**

The liquid-state electrode based on methyl green lauryl sulphate was found to behave in a nearly Nernstian manner towards the lauryl sulphate anion. The electrode needed to be conditioned overnight in a $10^{-3}$ M sodium lauryl sulphate solution. The potential drift was 38.6 mV 5 days after preparation of the electrode. A steady potential response was obtained for $10^{-2}$ to $10^{-4}$ M concentration of lauryl sulphate within 2 minutes and after longer periods at lower concentrations.

The liquid-state electrode based on Methylene Blue Manoxol OT did not behave in a Nernstian manner. The surfactant (Manoxol OT) seemed to wash out the basic dye complex from the rubber as the solution gradually turned blue in colour. The colour of the rubber after 5 days was similar to the colour of the rubber before being swelled in the organic basic dye solution. This indicates that the membrane had lost the active material after five days.

The responses of the two electrodes to the relevant anions are listed in Tables 11 and 12 and are shown graphically in Fig 8.

**Studying the Interferences**

There was no significant interference from sulphate, chloride, phosphate or urea. Nitrate at $10^{-2}$ M gave response very near to that
### TABLE 11
Response of the Methyl Green lauryl sulphate electrode to lauryl sulphate.

<table>
<thead>
<tr>
<th>Lauryl Sulphate Conc. (M)</th>
<th>Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-2}$</td>
<td>-152.0</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>-104.7</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>-48.9</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>+0.1</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>+36.2</td>
</tr>
</tbody>
</table>

### TABLE 12
Response of the Methylene Blue Manoxol OT electrode to Manoxol OT anion.

<table>
<thead>
<tr>
<th>Manoxol OT</th>
<th>Conc. (M)</th>
<th>pH</th>
<th>Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$2 \times 10^{-3}$</td>
<td>2.699</td>
<td>-75.0</td>
</tr>
<tr>
<td></td>
<td>$2 \times 10^{-4}$</td>
<td>3.699</td>
<td>-55.3</td>
</tr>
<tr>
<td></td>
<td>$2 \times 10^{-5}$</td>
<td>4.699</td>
<td>-22.0</td>
</tr>
<tr>
<td></td>
<td>$2 \times 10^{-6}$</td>
<td>5.699</td>
<td>-3.1</td>
</tr>
<tr>
<td></td>
<td>$2 \times 10^{-7}$</td>
<td>6.699</td>
<td>+12.0</td>
</tr>
</tbody>
</table>
**Fig 8**

**ELECTRODE RESPONSE TO SURFACTANT**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Methyl Green lauryl sulphate</td>
<td>lauryl sulphate anion</td>
</tr>
<tr>
<td>(ii) Methylene Blue Manoxol OT</td>
<td>Manoxol OT anion</td>
</tr>
</tbody>
</table>
obtained with $10^{-2}$ M lauryl sulphate but the potential versus $\mathrm{pNO}_3$ slope was considerably less than Nernstian (10 mV per decade in the $\mathrm{pNO}_3$ range of 2 to 4). The effect of pH on the electrode performance was studied. It was found that the electrode response is affected above pH 4.

Application of Methyl Green Lauryl Sulphate in Potentiometric Titration

A solution of $10^{-3}$ M lauryl sulphate was titrated with $10^{-3}$ M solution of cetyltrimethylammonium bromide (CTAB). The end point was determined by means of first derivative and was satisfactorily reproducible. Potential-volume data for the titration is given in Table 13 and shown in Figs 9 and 10.

DISCUSSION

The liquid state electrode based on Methyl Green lauryl sulphate is suitable for the determination of the lauryl sulphate anion and some other anion surfactants. For example, the electrode responds to lauryl benzene sulphonate in a similar manner to its response to lauryl sulphate. Although the electrode responded in a nearly Nernstian manner in the range of $10^{-3}$ to $10^{-4}$ M lauryl sulphate, the response is slightly less than that at higher and lower concentrations. In any case, the electrode can be used successfully in potentiometric titrations of anion surfactant with cationic surfactant. Although the potential drifts in one particular direction, the reproducibility is quite good in a particular day (within 1 mV) after the first day of preparation. The electrode was used satisfactorily for two weeks and there is no reason why it should not be valid for a
<table>
<thead>
<tr>
<th>Amount of Titrant added in mls.</th>
<th>Potential (mV)</th>
<th>$\Delta E/\Delta V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>62</td>
<td>1.1</td>
</tr>
<tr>
<td>10</td>
<td>73</td>
<td>1.2</td>
</tr>
<tr>
<td>20</td>
<td>85</td>
<td>1.6</td>
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<tr>
<td>30</td>
<td>101</td>
<td>2.1</td>
</tr>
<tr>
<td>40</td>
<td>122</td>
<td>3.5</td>
</tr>
<tr>
<td>42</td>
<td>129</td>
<td>4.0</td>
</tr>
<tr>
<td>44</td>
<td>137</td>
<td>5.0</td>
</tr>
<tr>
<td>46</td>
<td>147</td>
<td>6.0</td>
</tr>
<tr>
<td>49</td>
<td>169</td>
<td>10.0</td>
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<tr>
<td>50</td>
<td>182</td>
<td>14.0</td>
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<td>51</td>
<td>200</td>
<td>18.0</td>
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<td>52</td>
<td>235</td>
<td>35.0</td>
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<td>53</td>
<td>296</td>
<td>61.0</td>
</tr>
<tr>
<td>54</td>
<td>325</td>
<td>29.0</td>
</tr>
<tr>
<td>56</td>
<td>360</td>
<td>17.5</td>
</tr>
<tr>
<td>57</td>
<td>371</td>
<td>11.0</td>
</tr>
<tr>
<td>60</td>
<td>396</td>
<td>6.6</td>
</tr>
<tr>
<td>65</td>
<td>418</td>
<td>4.4</td>
</tr>
<tr>
<td>70</td>
<td>426</td>
<td>0.8</td>
</tr>
</tbody>
</table>

**TABLE 13** Potentiometric titration of 50 ml of $10^{-3}$ M lauryl sulphate with $10^{-3}$ M CTAB.
Fig 9

POTENTIOMETRIC TITRATION OF 50 ML OF $10^{-3}$ M SODIUM LAURYL SULPHATE WITH $10^{-3}$ M CTAB.
DETECTION OF END POINT OF SURFACTANT TITRATION USING A FIRST DERIVATIVE GRAPH
longer period of time. The solution has to be buffered as the electrode is responsive to pH variation outside the range of 2 to 4.

The liquid state electrode based on Methylene Blue Manoxol OT does not seem very promising as the active material gradually dissolved in the aqueous phase. In fact, Manoxol OT is a strong detergent and this factor may contribute in stripping the active material from the organic phase when the electrode is in contact with Manoxol OT. Storing the electrode in distilled water did not improve the electrode performance as the active material is also gradually dissolved in water. A PVC membrane electrode based on the Methylene Blue Manoxol OT did not give better results. Although Methylene Blue is successfully used in spectrophotometric procedures for determining less than 100 µg/l of anionic detergent \(^{(102)}\), the compound does not seem to be suitable as an active material for surfactant ion selective electrodes.
INTRODUCTION

Basic dye colorimetric procedures for determining indium(III) and iron(III) have received little attention in the literature. Brilliant Green has been used to extract tetrabromoindate(III) by Lîteanu and Cordos. Further studies by Fogg et al concluded that Brilliant Green is not a suitable reagent for the determination of indium. Likussar et al. used Crystal Violet to extract FeCl₄⁻ from 4 M hydrochloric acid. The structure of Crystal Violet is shown below.

In the present work, Crystal Violet (Basic Violet 3, C.I. 42555) has been used in an attempt to extract tetrachloroindate(III) or tetrabromoindate(III). The basic dye complexes in the organic phase have been used in preparing electrodes responsive to InCl₄⁻ or InBr₄⁻. The response of the electrodes to FeCl₄⁻ or FeBr₄⁻ has been investigated.

As triphenylmethylarsenium thiocyanate was recommended for
gravimetric determination of iron(III) in the range of 1 to 10 µg per ml (188). (Ph₃FeAs)₃Fe(SCN)₆ has been investigated for use as an active material in an ion-selective electrode responsive to $[\text{Fe(SCN)}_6]^{3-}$.

The Indium complex was also investigated.

EXPERIMENTAL

Preparation of Crystal Violet Tetrachloroindate(III) and Tetrabromoindate(III)

Although Schufte (184) has shown that the InCl₄⁻ complex is formed in hydrochloric acid solution of concentration higher than 8M, in the present work, the extraction was made from 3M hydrochloric acid solution into o-dichlorobenzene or into 1:1 o-dichlorobenzene:nitrobenzene. 20 ml of 10⁻³ M indium(III) sulphate, 20 ml of 10⁻³ M Crystal Violet and 25 ml of the organic solvent were used in every extraction.

Tetrabromoindate(III) salt of Crystal Violet was extracted from 1M potassium bromide into dichlorobenzene. The amounts of the reagents used were similar to those mentioned above in the extraction of Crystal Violet tetrachloroindate.

Preparation of (Ph₃FeAs)₃Fe(SCN)₆

The compound was prepared according to Dwyer and Gibson (188) as follows. Triphenylmethylarsonium chloride (55 ml of 5% solution) was mixed to sufficient water (800 ml), and to the mixture was added slowly a solution of ferric alum (1.06 g in 5 ml of 2½ H₂SO₄). The finely divided precipitate that separated was coagulated by stirring and
after filtration was washed with 0.01N H₂SO₄ solution.

The indium compound was prepared similarly by using indium sulphate instead of ferric alum.

**Preparation and Use of the Liquid-State Membrane**

The liquid-state membrane was prepared, as mentioned before, by soaking natural rubber in the appropriate solution of the organic complex overnight. The membranes were used in the electrode assembly, described before. Potential measurements were made with a Radiometer PHM64 Research pH meter versus a saturated calomel reference electrode. The electrodes were conditioned in a 10⁻³ M solution of the ion to be tested.

**RESULTS**

The electrode based on Crystal Violet Salt tetrabromoindate responded to InBr₄⁻ and FeBr₄⁻ in 1M potassium bromide while the electrode based on tetrachloroindate responded to InCl₄⁻ and FeCl₄⁻ in 3M hydrochloric acid. Although none of the electrodes gave full Nernstian response the electrodes can be used as the reproducibility in one particular day is quite good, within 1 mV, and a steady potential reading is obtained within 3 minutes. The potential of any of the electrodes drifted in one particular direction and the extent of the drift depended on the dye salt and the organic solvent used. An electrode based on Crystal Violet tetrachloroindate in o-dichlorobenzene showed a potential drift of 74 mV after 8 days of preparation while an electrode based on Crystal Violet tetrachloroindate in 1:1
o-dichlorobenzene:nitrobenzene showed a potential drift of 29 mV after the same period of time. The Crystal Violet tetrabromoindate electrode showed a potential drift of 117 mV after 3 days and further drift of 9 mV after the following 13 days. The InBr$_4^-$ electrode had to be conditioned for two hours in the solution of FeBr$_4^-$ before it gave a steady response to FeBr$_4^-$. The results obtained with these electrodes are listed in Table 14 and are shown graphically in Fig 11.

Liquid-state electrodes based on (Ph$_3$As)$_3$Fe(SCN)$_6$ and (Ph$_3$MeAs)$_3$In(SCN)$_6$ did not respond to either Re(SCN)$_6^{3-}$ or In(SCN)$_6^{3-}$. The electrodes responded to thiocyanate, perchlorate and to a lesser extent to nitrate. The results are listed in Table 15.

**Study of Interfering Ions**

The following ions, Cu$^{2+}$, Zn$^{2+}$, Na$^+$, Ni$^{2+}$, SO$_4^{2-}$ and NO$_3^-$, did not interfere in the determination of indium in 1M potassium bromide using the electrode based on Crystal Violet tetrabromoindate. Perchlorate and perrhenate interfered as well as mercury(II) in 1M KBr. The response of the electrode to these ions is listed in Table 16. The selectivity constants are calculated at 10$^{-3}$ and 10$^{-5}$M using the equation

$$\log K_{\text{InBr}_4^-/\text{Interfering Ion}} = \frac{E_1 - E_2}{2.303 \, RT/F}$$

where $E_1$ is the potential of the electrode for the primary ion and $E_2$ is the potential of the electrode for the interfering ion. The selectivity constants are listed in Table 17.
<table>
<thead>
<tr>
<th>Ion Conc. (M)</th>
<th>$\text{InCl}_4^-$</th>
<th>$\text{FeCl}_4^-$</th>
<th>$\text{InCl}_4^-$</th>
<th>$\text{FeCl}_4^-$</th>
<th>$\text{InBr}_4^-$</th>
<th>$\text{FeBr}_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-2}$</td>
<td>$-29.9$</td>
<td>-</td>
<td>+86.0</td>
<td>+38.3</td>
<td>+94.5</td>
<td>+149.6</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>+25.7</td>
<td>-78.5</td>
<td>+146.1</td>
<td>+32.3</td>
<td>+149.6</td>
<td>+148.1</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>+58.2</td>
<td>-18.6</td>
<td>+185.2</td>
<td>+92.1</td>
<td>+201.6</td>
<td>+197.7</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>+66.2</td>
<td>+31.9</td>
<td>+206.1</td>
<td>+148.2</td>
<td>+243</td>
<td>+231.4</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>+61.3</td>
<td>+61.3</td>
<td>+207.3</td>
<td>+173.0</td>
<td>+252</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 14** Potential Response (mV) of electrodes based on Crystal Violet tetrachloroindate and Crystal Violet tetrabromoindate to $\text{InCl}_4^-$, $\text{FeCl}_4^-$, $\text{InBr}_4^-$, and $\text{FeBr}_4^-$. 
The Electrode

(i) Crystal Violet tetrachloroindate in
    o-dichlorobenzene
(ii) Crystal Violet tetrachloroindate in
     o-dichlorobenzene
(iii) Crystal Violet tetrachloroindate in 1:1
     o-dichlorobenzene : nitrobenzene
(iv) Crystal Violet tetrachloroindate in 1:1
     o-dichlorobenzene : nitrobenzene
(v)  Crystal Violet tetrabromoindate in
     o-dichlorobenzene

Ion

FeCl₄⁻

InCl₄⁻

FeCl₄⁻

InCl₄⁻

InBr₄⁻
### TABLE 16: Response of an electrode based on tetrabromoindate to ClO$_4^-$, ReO$_4^-$ and HgBr$_3^-$

<table>
<thead>
<tr>
<th>Ion Concentration (M)</th>
<th>ClO$_4^-$ Potential (mV)</th>
<th>ReO$_4^-$ Potential (mV)</th>
<th>HgBr$_3^-$ Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10$^{-1}$</td>
<td>+132.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10$^{-2}$</td>
<td>+186.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10$^{-3}$</td>
<td>+240.9</td>
<td>+228.4</td>
<td>+172.0</td>
</tr>
<tr>
<td>10$^{-4}$</td>
<td>+295.2</td>
<td>+282.9</td>
<td>+222.5</td>
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<tr>
<td>10$^{-5}$</td>
<td>+335.0</td>
<td>+328.0</td>
<td>+262.0</td>
</tr>
<tr>
<td>10$^{-6}$</td>
<td>+351.1</td>
<td>+353.1</td>
<td>+279.0</td>
</tr>
</tbody>
</table>

### TABLE 17: Selectivity constant (K$_{InBr_3^-/Interf. Ions}$)

<table>
<thead>
<tr>
<th>Interfering Ion</th>
<th>Selectivity Constant (10$^{-3}$ M)</th>
<th>Selectivity Constant (10$^{-5}$ M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO$_4^-$</td>
<td>2.8 x 10$^{-2}$</td>
<td>4.8 x 10$^{-3}$</td>
</tr>
<tr>
<td>ReO$_4^-$</td>
<td>4.8 x 10$^{-2}$</td>
<td>6.3 x 10$^{-3}$</td>
</tr>
<tr>
<td>HgBr$_3^-$</td>
<td>4.3 x 10$^{-1}$</td>
<td>4.2 x 10$^{-2}$</td>
</tr>
</tbody>
</table>

TABLE 16: Response of an electrode based on tetrabromoindate to ClO$_4^-$, ReO$_4^-$ and HgBr$_3^-$.

TABLE 17: Selectivity constant (K$_{InBr_3^-/Interf. Ions}$).
<table>
<thead>
<tr>
<th>Ion Concentration (M)</th>
<th>((\text{Ph}_3\text{MeAs})_3\text{Fe(SCN)}_6) in dichlorobenzene electrode</th>
<th>((\text{Ph}_3\text{MeAs})_3\text{In(SCN)}_6) in 1:1 dichlorobenzene-nitrobenzene electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SCN(^-)</td>
<td>Cl(_4^+)</td>
</tr>
<tr>
<td>10(^{-1})</td>
<td>-134.9</td>
<td>-98.9</td>
</tr>
<tr>
<td>10(^{-2})</td>
<td>-98.9</td>
<td>-116.1</td>
</tr>
<tr>
<td>10(^{-3})</td>
<td>-56.4</td>
<td>-64.4</td>
</tr>
<tr>
<td>10(^{-4})</td>
<td>-16.6</td>
<td>-19.0</td>
</tr>
<tr>
<td>10(^{-5})</td>
<td>+8.5</td>
<td>+31.2</td>
</tr>
<tr>
<td>10(^{-6})</td>
<td>+9.3</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 15** Potential response (mV) of electrodes based on iron and indium salts of triphenylmethylenarsionum thiocyanate to SCN\(^-\), Cl\(_4^+\) and NO\(_3^-\).
DISCUSSION

Electrodes described above based on Crystal Violet tetrachloroindate(III) responded to InCl$_4^-$ and FeCl$_4^-$ while electrodes based on Crystal Violet tetrabromoindate responded to InBr$_4^-$ and to FeBr$_4^-$. The response is nearly Nernstian over a narrow range of concentration. The useful range for indium determination is from $10^{-2}$ M to $10^{-4}$ M when Crystal Violet tetrachloroindate electrode is used and from $10^{-2}$ M to $10^{-5}$ M when the Crystal Violet tetrabromoindate electrode is used. The useful range is slightly better for iron(III). The Crystal Violet tetrachloroindate electrode is more selective to FeCl$_4^-$ than to InCl$_4^-$ while the Crystal Violet tetrabromoindate electrode had almost the same selectivity toward InBr$_4^-$ and FeBr$_4^-$. ClO$_4^-$, ReO$_4^-$ and HgBr$_3^-$ interfere in the determination of iron and indium but Cu$^{2+}$, Zn$^{2+}$, Ni$^{2+}$, SO$_4^{2-}$ and NO$_3^-$ do not interfere.

It is recommended that the electrode be conditioned overnight in a $10^{-3}$ M solution of the ion to be measured as most of the potential drift occurs during the first 24 hours after electrode preparation. It is also recommended that the electrode be stored in a $10^{-3}$ M solution of the relevant ion. Storing the electrode in a solution having less than $10^{-5}$ M of the relevant ion or particularly in water is detrimental to the condition of the electrode. The temperature of the aqueous solution must be fixed at 25 ± 1 °C as an electrode based on Crystal Violet InCl$_4$ did not function at all when the temperature of the solution was raised to 45 °C.

As is generally the case with this type of electrode, the
potential (in a particular solution) drifts from day to day. The potential versus pIon remained unchanged. The reproducibility on one particular day was within 1mV, except during the first day of preparation.

For general use, Crystal Violet tetrachloroindate in 1:1 dichlorobenzene:nitrobenzene is recommended for the determination of iron in 3M hydrochloric acid as the electrode is 10 times more selective to FeCl$_4^-$ than to InCl$_4^-$ and the potential drift was not as bad as when dichlorobenzene was used alone as the organic solvent. Crystal Violet InBr$_4^-$ in dichlorobenzene is recommended for the determination of indium(III) in 1M potassium bromide as the electrode response is better for indium and the range is wider than for the two other electrodes.

Indium and iron salts of triphenylmethylarsionium thiocyanate were found not to be suitable for use as active materials for preparing electrodes responsive to In(SCN)$_6^{3-}$ and Fe(SCN)$_6^{3-}$. Electrodes based on these active materials responded to SCN$^-$, ClO$_4^-$ and NO$_3^-$. 
ELECTRODES SELECTIVE TO BRILLIANT GREEN AND CERTAIN AZO DYE ANIONS

INTRODUCTION

Methods available for quantitative determination of basic dye-stuffs were reviewed by Burgess, Fogg and Burns (189). These methods include those based on precipitating the basic dye by means of an acidic dye or with 12-tungstosilicic acid.

In the present work, Crystal Violet salts of certain azo dyes were investigated for use as active materials for electrodes selective to certain azo dye anions. Brilliant Green 12-tungstosilicate has been prepared and used for an electrode selective to Brilliant Green. The electrode has been used in studying the stability of Brilliant Green solutions.

EXPERIMENTAL

Preparation of Crystal Violet 4-(2-Pyridylazo)-resorcinol

A solution of Crystal Violet (10^{-2} M) was used to precipitate 4-(2-Pyridylazo)-resorcinol (PAR) from 10^{-2} M solution. The precipitate was filtered, washed with distilled water and dried at room temperature.

Crystal Violet Solochrome Violet RS has been prepared similarly.
Preparation of Brilliant Green 12-Tungstosilicate

Brilliant Green 12-tungstosilicate was prepared according to Burgess, Fogg and Burns (189) by dissolving 0.5 g of Brilliant Green in 50 ml of distilled water and heating the solution to 70 °C. Then 5 ml of concentrated hydrochloric acid was added and 100 ml of 10⁻² M 12-tungstosilicic acid with stirring. The precipitate was left for 1 hour at room temperature, then filtered, washed with distilled water and dried at 100 °C.

Preparation of the Membrane and the Use of the Electrode

Membranes used in these studies were prepared, as mentioned before, by soaking the natural rubber discs in a saturated solution of the appropriate organic salt in o-dichlorobenzene overnight. The membrane was fixed in the electrode body described before. Potential measurements were made with a Radiometer PHM64 Research pH meter versus a saturated calomel electrode.

RESULTS

A liquid state electrode based on Crystal Violet PAR was found to respond to PAR, Solochrome Violet RS and Orange IV anions. The response to PAR and Orange IV anions was found to be Nernstian over a narrow range (of 10⁻³ to 10⁻⁴ M) and less than that at higher and lower concentrations. The response to Solochrome Violet RS anion was less than Nernstian.

The liquid state electrode based on Crystal Violet Solochrome
Violet RS responded in a Nernstian manner to Orange IV anion and Brilliant Green cation over a narrow range of concentration, $10^{-3}$ to $10^{-4}$ M and $10^{-4}$ to $10^{-5}$ M respectively. The response was less than Nernstian at higher and lower concentrations of Orange IV and Brilliant Green. The response to PAR and Solochrome Violet RS was also less than Nernstian.

The response of the liquid state electrode based on Brilliant Green 12-tungstosilicate was found to be nearly Nernstian to the Brilliant Green cation. The response to freshly prepared solutions of Brilliant Green was quite different from that obtained with solutions prepared 24 hours previously. Buffering the Brilliant Green solution narrows the difference.

All the electrodes needed conditioning overnight in the solution of the ion to be measured. The electrodes gave steady responses within 2 minutes. The electrode potential drifted in one particular direction and the extent of the drift depended on the active material used. The Crystal Violet PAR electrode showed an overall drift of 6.5 mV after 14 days and 15 mV after 27 days of preparation. The Crystal Violet Solochrome Violet RS electrode showed a potential drift of 138 mV after 24 hours of preparation and a further 2 mV after 14 days of preparation. The slope of the potential versus plon concentration remained unchanged after more than four weeks. The results obtained using these electrodes are listed in Tables 18 and 19 and are shown graphically in Fig 12.
<table>
<thead>
<tr>
<th>Ion Conc. (m)</th>
<th>Crystal Violet PAR Electrode (in o-dichlorobenzene)</th>
<th>Crystal Violet Solochrome Violet RS Electrode (in o-dichlorobenzene)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PAR</td>
<td>Solochrome Violet RS</td>
</tr>
<tr>
<td>10^{-2}</td>
<td>+196.2</td>
<td>+165.6</td>
</tr>
<tr>
<td>10^{-3}</td>
<td>+244.9</td>
<td>+193.2</td>
</tr>
<tr>
<td>10^{-4}</td>
<td>+304.0</td>
<td>+240.3</td>
</tr>
<tr>
<td>10^{-5}</td>
<td>+349.6</td>
<td>+290.4</td>
</tr>
<tr>
<td>10^{-6}</td>
<td>+365.2</td>
<td>+321.1</td>
</tr>
<tr>
<td>10^{-7}</td>
<td>+368.2</td>
<td>+327.6</td>
</tr>
</tbody>
</table>

**TABLE 1B** Potential response (mV) of electrodes based on PAR and Solochrome Violet RS salts of Crystal Violet to PAR, Solochrome Violet RS and Orange IV anions and to the Brilliant Green cation.
| Brilliant Green Conc. (M) | Potential (mV) | | | | |
|---|---|---|---|---|
| 10^{-3} | +402.5 | +362.2 | +412.1 | +400.2 |
| 10^{-4} | +345.0 | +324.1 | +354.4 | +349.0 |
| 10^{-5} | +287.3 | +286.2 | +303.1 | +302.4 |
| 10^{-6} | +240.1 | +248.9 | +280.2 | +281.1 |

**TABLE 19** Response of electrode based on Brilliant Green 12-tungstosilicate to Brilliant Green cation.
ELECTRODE RESPONSE TO DYE IONS

The Electrode

(i) Solochrome Violet Crystal Violet
(ii) Solochrome Violet Crystal Violet
(iii) Solochrome Violet Crystal Violet
(iv) PAR Crystal Violet
(v) PAR Crystal Violet
(vi) PAR Crystal Violet
(vii) Solochrome Violet RS Crystal Violet

The Ion

Orange IV
Solochrome Violet RS
PAR
Orange IV
Solochrome Violet RS
PAR
Brilliant Green

Fig 12
Studying the Interferences

The interference by certain ions was studied using either the electrode based on Crystal Violet Solochrome Violet RS or the one based on Brilliant Green 12-tungstosilicate. Fe$^{3+}$, In$^{3+}$, Sb$^{3+}$, Cu$^{2+}$, Zn$^{2+}$, Ni$^{2+}$, Na$^+$, K$^+$, SO$_4^{2-}$ and Cl$^-$ were found not to interfere in the measurement but ClO$_4^-$, SCN$^-$ and nitrate were found to interfere. The response of the two electrodes to these ions is listed in Table 20.

It can be seen from Tables 18 and 20 that the selectivity of Crystal Violet Solochrome Violet RS electrode for the tested ion at 10$^{-3}\text{M}$ concentration is in the order Orange IV $>$ Solochrome Violet RS $>$ perchlorate $>$ PAR $>$ thiocyanate $>$ nitrate. As the electrode is not very selective to any of these anions, the determination of one anion can be achieved only in the absence of the other anions.

Studying the pH Effects on the Electrode Response

pH has a great influence on the observed response of the present electrodes. The effect of pH of the test solution on the electrode potential was studied using both the Crystal Violet Solochrome Violet RS electrode and the Brilliant Green 12-tungstosilicate electrode. The results are listed in Table 21 and are shown graphically in Fig 13.

Studying the Stability of Brilliant Green Solutions

Priestman$^{(190)}$ observed that Brilliant Green solutions were slow to reach a maximum absorbance value when diluted to the point where their absorbance values could be measured in 1 cm cells. This was attributed to de-dimerisation of the Brilliant Green. Further studies by Ullcox$^{(191)}$ showed that the absorbance of 1.03 x 10$^{-3}\text{M}$
<table>
<thead>
<tr>
<th>Ion Conc. (M)</th>
<th>Crystal Violet Solochrome Violet RS Electrode</th>
<th>Brilliant Green 12-Tungstosilicate Electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{ClO}_4^-$</td>
<td>$\text{SCN}^-$</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>- 6.2</td>
<td>+ 30.2</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>+ 44.8</td>
<td>+ 81.1</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>+ 101.2</td>
<td>+ 128.3</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>+ 153.9</td>
<td>+ 172.2</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>+ 201.0</td>
<td>+ 214.2</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>+ 223.2</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 20** Potential response (mV) of electrodes based on Crystal Violet Solochrome Violet RS and Brilliant Green 12-tungstosilicate to $\text{ClO}_4^-$, $\text{SCN}^-$ and $\text{NO}_3^-$. 
<table>
<thead>
<tr>
<th>pH</th>
<th>Potential (mV)</th>
<th>pH</th>
<th>Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.058</td>
<td>+ 93.1</td>
<td>10.993</td>
<td>+ 3.9</td>
</tr>
<tr>
<td>10.058</td>
<td>+ 133.3</td>
<td>10.018</td>
<td>+ 63.1</td>
</tr>
<tr>
<td>8.925</td>
<td>+ 191.7</td>
<td>9.082</td>
<td>+ 110.2</td>
</tr>
<tr>
<td>7.814</td>
<td>+ 258.9</td>
<td>7.866</td>
<td>+ 158.1</td>
</tr>
<tr>
<td>6.992</td>
<td>+ 268.8</td>
<td>7.166</td>
<td>+ 180.1</td>
</tr>
<tr>
<td>5.998</td>
<td>+ 268.8</td>
<td>6.325</td>
<td>+ 219.1</td>
</tr>
<tr>
<td>4.821</td>
<td>+ 268.9</td>
<td>5.093</td>
<td>+ 252.0</td>
</tr>
<tr>
<td>4.001</td>
<td>+ 270.2</td>
<td>4.115</td>
<td>+ 255.8</td>
</tr>
<tr>
<td>3.060</td>
<td>+ 275.3</td>
<td>2.820</td>
<td>+ 256.6</td>
</tr>
<tr>
<td>2.089</td>
<td>+ 280.6</td>
<td>2.312</td>
<td>+ 255.1</td>
</tr>
<tr>
<td>2.037</td>
<td></td>
<td>2.037</td>
<td>+ 252.1</td>
</tr>
</tbody>
</table>
**Figure 13**

ELECTRODE RESPONSE TO pH

(i) Brilliant Green 12-tungstosilicate electrode

(ii) Crystal Violet Solochrome Violet electrode
Brilliant Green solution was much higher when the measurement was taken immediately after preparing it from the solid than the absorbance of the same solution after being stored for 18 hours. The absorbance of a 1.03 x 10^{-5} M solution prepared from the solid immediately before the measurement is also much higher than the absorbance of a solution prepared from 1.03 x 10^{-3} M solution, which was stored for 18 hours, by diluting the concentrated solution. The absorbance of a 1.03 x 10^{-5} M solution immediately prepared from the solid before the measurement was slightly higher than the absorbance of the same solution after it was stored for 42 hours. The explanation suggested that during the period of storage in concentrated aqueous solution, a Brilliant Green dimer is formed slowly, and thus slowly de-dimerises upon dilution.

During the present work, the stability of the Brilliant Green solution was studied by following the change in the potential of the electrode when buffered or unbuffered solutions of 10^{-3} M, 10^{-4} M and 10^{-5} M Brilliant Green were tested. It was found that when a 10^{-3} M solution, which was directly prepared from solid was tested, the potential of the electrode decreased slowly until it has reached a constant value. The decrease in the potential is less when the solution was buffered, using acetic acid sodium acetate buffer. The potential decrease was also less when a 10^{-4} M Brilliant Green solution, prepared from solid was tested. On the other hand, the potential of 10^{-4} and 10^{-5} M Brilliant Green solutions, prepared by diluting the stored solution of 10^{-3} M, was increased slowly to reach a constant value. The results obtained in these studies, using the electrode based on Brilliant Green 12-tungstosilicate, are listed in Tables 22, 23 and 24, and are shown graphically in Fig 14.
<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Potential (mV)</th>
<th>Time (min)</th>
<th>Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>412.0</td>
<td>1</td>
<td>+402.5</td>
</tr>
<tr>
<td>3</td>
<td>411.9</td>
<td>8</td>
<td>+400.1</td>
</tr>
<tr>
<td>30</td>
<td>411.5</td>
<td>15</td>
<td>+397.3</td>
</tr>
<tr>
<td>134</td>
<td>407.8</td>
<td>23</td>
<td>+394.8</td>
</tr>
<tr>
<td>199</td>
<td>406.4</td>
<td>35</td>
<td>+390.4</td>
</tr>
<tr>
<td>309</td>
<td>404.4</td>
<td>45</td>
<td>+389.1</td>
</tr>
<tr>
<td>15 hours</td>
<td>400.1</td>
<td>55</td>
<td>+385.5</td>
</tr>
<tr>
<td>17 hours</td>
<td>400.2</td>
<td>70</td>
<td>+382.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>90</td>
<td>+378.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>110</td>
<td>+375.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>130</td>
<td>+373.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
<td>+371.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>210</td>
<td>+366.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>240</td>
<td>+364.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260</td>
<td>+363.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>280</td>
<td>+362.0</td>
</tr>
<tr>
<td>20 hours</td>
<td></td>
<td></td>
<td>+359.0</td>
</tr>
<tr>
<td>22 hours</td>
<td></td>
<td></td>
<td>+359.0</td>
</tr>
</tbody>
</table>

**TABLE 22** Response of the electrode to Brilliant Green solutions, directly prepared from the solid, as a function of time.
<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Potential (mV)</th>
<th>Time (min)</th>
<th>Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>+354.9</td>
<td>1</td>
<td>+344.9</td>
</tr>
<tr>
<td>10</td>
<td>+354.1</td>
<td>4</td>
<td>+344.5</td>
</tr>
<tr>
<td>22</td>
<td>+353.4</td>
<td>9</td>
<td>+343.8</td>
</tr>
<tr>
<td>37</td>
<td>+352.8</td>
<td>16</td>
<td>+342.9</td>
</tr>
<tr>
<td>50</td>
<td>+352.4</td>
<td>34</td>
<td>+340.3</td>
</tr>
<tr>
<td>70</td>
<td>+351.8</td>
<td>50</td>
<td>+337.5</td>
</tr>
<tr>
<td>80</td>
<td>+351.3</td>
<td>70</td>
<td>+335.0</td>
</tr>
<tr>
<td>105</td>
<td>+350.8</td>
<td>85</td>
<td>+333.5</td>
</tr>
<tr>
<td>200</td>
<td>+349.9</td>
<td>105</td>
<td>+331.6</td>
</tr>
<tr>
<td>20 hours</td>
<td>+349.0</td>
<td>165</td>
<td>+328.7</td>
</tr>
<tr>
<td>22 hours</td>
<td>+349.1</td>
<td>180</td>
<td>+326.4</td>
</tr>
</tbody>
</table>

**TABLE 23** Response of the electrode to Brilliant Green solution, directly prepared from solid, as a function of time.
TABLE 24  Response of the electrode to Brilliant Green solutions, prepared by diluting a stored concentrated reagent solution that had been stored for 24 hours, as a function of time.

<table>
<thead>
<tr>
<th>10^{-4} M Brilliant Green unbuffered solution</th>
<th>10^{-5} M Brilliant Green unbuffered solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min)</td>
<td>Potential (mV)</td>
</tr>
<tr>
<td>1</td>
<td>+306.6</td>
</tr>
<tr>
<td>3</td>
<td>+307.6</td>
</tr>
<tr>
<td>13</td>
<td>+310.7</td>
</tr>
<tr>
<td>20</td>
<td>+313.1</td>
</tr>
<tr>
<td>30</td>
<td>+315.8</td>
</tr>
<tr>
<td>40</td>
<td>+318.0</td>
</tr>
<tr>
<td>60</td>
<td>+321.1</td>
</tr>
<tr>
<td>70</td>
<td>+322.0</td>
</tr>
<tr>
<td>85</td>
<td>+323.0</td>
</tr>
<tr>
<td>105</td>
<td>+323.9</td>
</tr>
<tr>
<td>125</td>
<td>+324.2</td>
</tr>
<tr>
<td>140</td>
<td>+324.3</td>
</tr>
<tr>
<td>200</td>
<td>+324.5</td>
</tr>
<tr>
<td>20 hours</td>
<td>+324.6</td>
</tr>
</tbody>
</table>
RESPONSE OF ELECTRODE BASED ON BRILLIANT GREEN 12-TUNGSTOSILICATE TO R⁺ AS A FUNCTION OF TIME

(i) 10⁻⁵M unbuffered solution  (ii) 10⁻⁴M unbuffered solution  (iii) 10⁻⁴M unbuffered solution
(iv) 10⁻⁴M buffered solution  (v) 10⁻³M unbuffered solution  (vi) 10⁻³M buffered solution

*\textit{Solutions (i) and (ii) were prepared by dilution of concentrated solution and the rest were prepared directly from solid.}
DISCUSSION

The electrodes described do not respond in a fully Nernstian manner over a wide range of concentrations of dye ion to be measured. The electrodes however may find applications in determining those dyes, which were studied here, as the potential slope versus pIon remained unchanged after three weeks.

As is generally the case with this type of electrode, the potential in a particular solution drifts from day to day. The Crystal Violet PAR electrode showed an overall drift of 6.5 mV after 14 days and 15 mV after 27 days of the electrode preparation. The Crystal Violet Solochrome Violet RS electrode showed an overall drift of 138 mV after 24 hours of preparation and further 2 mV after 14 days of preparation. Therefore, it is recommended that the electrodes are conditioned overnight before use and are stored in $10^{-3}$ M solutions of the relevant ion.

As is generally the case with most of the electrodes based on basic dye salts, perchlorate, thiocyanate and nitrate interfere with the determination of the primary ion. It was found that the selectivities of the present electrodes were in the order Orange IV $>$ Solochrome Violet RS $>$ perchlorate $>$ PAR $>$ thiocyanate $>$ nitrate. This means that the determination of one anion can be achieved only in the absence of the other anions.

The pH of the solution is very important, firstly, because the electrodes respond to hydroxyl ion at high concentrations and,
secondly, because the dye can be determined only when it is in the form of a singly-charged ion. Around neutral pH (a pH of between 4 and 8), the Crystal Violet Solochrome Violet RS electrode is not affected by the change of the pH of the solution. In this range of pH, most of the acid dyes are present as single anions. For example, PAR is present as a single anion between pH 6 and 12. Brilliant Green 12-tungstosilicate electrode has a much narrower useful pH range (between 5 and 3) which means that the solution of Brilliant Green has to be buffered during the measurement. Sodium acetate-acetic acid buffer (pH of 4.7) was used in the present work. At this value of pH, Brilliant Green is present as a singly-charged cation.

Studying the stability of a Brilliant Green solution is an example of the successful application of those electrodes which do not give full Nernstian response over a wide range of concentration. In this study, it was found that at high concentrations of Brilliant Green the free ions present decreased on standing after preparing it from the salt, especially when the solution was not buffered, until it reached a constant value. On the other hand, the concentration of the free ions present increased upon the dilution of the concentrated solution. This supports the assumption by Willcox (191) that during the period of storage in concentrated aqueous solution, a Brilliant Green dimer is formed slowly, which slowly de-dimerises upon dilution.

Brilliant Green 12-tungstosilicate is recommended for general use as an active material for preparing electrodes selective to
Brilliant Green. The other two materials are recommended for preparing electrodes selective to acidic dye anions when the determination is required at a concentration in the useful range of the electrode response.
INTRODUCTION

Attempts were made to develop electrodes selective to saccharinate, copper(II) and sulphate. These attempts were not successful and these studies are described only briefly here.

Attempts at Developing an Electrode for Saccharinate

Methylene Blue has been used as a reagent in a spectrophotometric method for determination of saccharinate (192, 193). Methylene Blue saccharinate was prepared according to Shin and Tearé (192). The salt has been used in preparing liquid state PVC and silicone-rubber membrane electrodes. The liquid-state membrane electrode gave responses of 55.3 mV and 20 mV between the ranges $10^{-2}$ to $10^{-3}$ M and $10^{-3}$ to $10^{-4}$ M saccharinate respectively. The potential reading at $10^{-4}$ M solution was not stable and the dye salt started to dissolve in the aqueous solution. Steady response at $10^{-3}$ M and $10^{-4}$ M was achieved after 15 minutes. In spite of keeping the electrode in a $10^{-2}$ M saccharinate solution, the active material gradually dissolved in the aqueous solution. After 6 days of preparation, the electrode did not function at all. The silicone-rubber membrane electrode gave 22 mV potential slope between $10^{-2}$ and $10^{-3}$ M saccharinate and steady response was not achieved completely. The aqueous solution, in which the electrode was stored, turned blue in two days indicating gradual dissolution of the active material in the aqueous phase from the
membrane. The PVC membrane electrode behaved in a similar manner to the silicone-rubber membrane electrode.

It is believed that the solubility of Methylene Blue Saccharinate from the membrane into the aqueous solution is responsible for the unsatisfactory behaviour of the electrode. Ethylene dichloride, which was used in the colorimetric procedure, could not be used as solvent for preparing the liquid membrane because it is volatile. The absorbance of ethylene dichloride phase versus the square root of the concentration was linear and not that versus the concentration. This indicates incomplete extraction at lower concentrations of saccharinate.

**Attempt at Developing Electrodes Responsive to Copper(II)**

A sensitive spectrofluorimetric procedure for the determination of copper(II) in the range $1 - 6 \times 10^{-7}$ g was developed by Bailey et al. (194) utilising the ternary complex system Cu(Phen)$_2$Rose Bengal. In the present work, (Cu$_{1,10}$-phenanthroline)$_{2+}$Rose Bengal was extracted into either chloroform or dichlorobenzene according to the method described by Bailey et al. (194). A liquid state membrane electrode was prepared from the organic phase. The electrode based on the active material in chloroform gave a slope for the potential versus $pCu^{2+}$, in the presence of o-phenanthroline, of 12 and 11 mV in the range of $10^{-3}$ to $10^{-4}$ and $10^{-4}$ to $10^{-5}$ M copper(II) respectively. The electrode based on the active material in o-dichlorobenzene gave a potential slope versus $pCu^{2+}$ of 21.8 and 24.4 mV in the range of $10^{-3}$ to $10^{-4}$ and $10^{-4}$ to $10^{-5}$ M copper(II) respectively in the presence
of o-phenanthroline. The electrode did not give a reproducible result in one particular day and a steady potential reading was achieved only after 10 minutes.

Although complex formation is complete and fast, it is believed that the rate of dissociation of the complex is too slow which means that the rate of ion-exchange takes place slowly. In the spectrofluorimetric procedure ammoniacal acetone is added to break down the complex in the chloroform to liberate the free fluorescent Rose Bengal ion. This cannot be done to the organic phase from which the membrane of the electrode is to be prepared as it yields a product which can easily dissolve from the membrane into the aqueous solution.

**Attempt to develop an Electrode Responsive to Sulphate**

An attempt has been made to develop an ion-selective electrode responsive to sulphate using 2-aminoperimidine sulphate as an active material. Stephan et al.\(^\text{195-175}\) have used 2-aminoperimidine to determine small amounts of sulphate. The precipitate was prepared according to Stephan et al.\(^\text{195}\) and used to prepare liquid state and silicone rubber membrane electrodes. The material was also applied on the electrode. The results obtained with these electrodes are listed in Table 25.

The steady response was obtained after 10 minutes and the results were not reproducible.

It is believed that ion exchange between the membrane and the
solution takes place very slowly and this is responsible for the unsatisfactory behaviour of the electrode. The solubility of the compound in both dichlorobenzene and nitrobenzene is very small.

<table>
<thead>
<tr>
<th>$\text{SO}_4^{2-}$ Conc. (m)</th>
<th>Liquid Membrane in Dichlorobenzene</th>
<th>Liquid Membrane in 1:1 Dichlorobenzene-Nitrobenzene</th>
<th>Silicone Rubber Membrane</th>
<th>Selectrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-1}$</td>
<td>- 177.1</td>
<td>- 171.9</td>
<td>+ 188.0</td>
<td>+ 208.5</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>- 150.0</td>
<td>- 166.1</td>
<td>+ 195.0</td>
<td>+ 223.7</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>- 144.2</td>
<td>- 162.4</td>
<td>+ 195.0</td>
<td>+ 229.3</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 25** Potential response (mV) of electrodes based on 2-aminoperimidine sulphate to sulphate.
GENERAL DISCUSSION AND SUGGESTIONS FOR FURTHER WORK

The work described in this thesis has been concerned with the development and selection of organic salts for inclusion in ion-selective electrodes.

Basic dyes, which have been widely used for extractive photometric determinations of anions through formation of ion-association complexes, have been found to be very useful reagents in preparing organic salts for use as active materials for ion-selective electrodes. A liquid-state ion selective electrode assembly based on a natural rubber membrane, which was developed earlier in this laboratory, was found to be very suitable for applying these organic salts.

The correct choice of natural rubber for the membrane purpose is of great importance in producing an efficiently working electrode. The membrane has to be saturated with the ion-sensor solutions through absorption, and thus the rubber must be lightly cross-linked in order to take up the organic solvent solution. It has been observed that highly cross-linked natural rubbers seem to adsorb the dye salt only onto the surface and do not make good electroactive membranes. Electrodes with highly cross-linked natural rubber membranes have shown longer response time and larger potential drift. It appears that the dye salt must be uniformly distributed through the membrane; electrodes based on such membranes were found to respond very well towards their respective ions. It is convenient if the rubber matrix has the property of rapidly absorbing the dye salt solution. A natural rubber 2.7 mm in thickness was used for membrane purposes.
throughout the entire work. Thinner natural rubber membranes were found not to have good mechanical properties. A more systematic study on the natural rubber may be of great importance for the improvement of the performance of these electrodes. Improvements would include eliminating potential drifts, shortening response times and lengthening the useful working life of electrodes.

The correct choice of organic solvent is essential for ensuring a good solubility of the organic salt and a good performance of the electrode. The solvent used must be highly hydrophobic and in general must have a low dielectric constant and a high molecular weight. It should have a low vapour pressure to prevent significant evaporation and a sufficiently high viscosity. Also, it must be substantially inert to reaction with the electrode body. o-Dichlorobenzene was found to be a very suitable solvent. A mixture of dichlorobenzene and nitrobenzene was used when an organic salt had very low solubility in o-dichlorobenzene alone. Nitrobenzene alone could not be used as the rubber does not swell in it. The solubility, and the extractability of the dye salt increases with increasing dielectric constant of the solvent. In colorimetry, however, the use of high dielectric constant solvents is limited as the extractability of the basic dye reagent is also increased, resulting in high blank absorbances. In the absence of interferences, however, the use of organic solvents of high dielectric constant should not suffer from this disadvantage in ion-selective potentiometry using basic dyes, as the sample solution does not contain the basic dye reagent.

The choice of dye is also of great importance as the dye deter-
mines not only the selectivity to a particular anion but the solution conditions under which the electrode can be used. For example, Brilliant Green which is successfully used in colorimetry for determination of antimony, thallium and gold, cannot be used for preparing electrodes selective to these elements as the determinations have to be made at high hydrochloric acid concentrations. Under these conditions, the Brilliant Green undergoes further protonation. Sevron Red L, phenazinduline 0 and certain other basic dyes have been used successfully in preparing electrodes responsive to antimony and thallium; these dyes were not useful in the corresponding colorimetric determinations owing to high absorbance blanks. Saframine 0 has been used for preparing electrodes selective to gold. Methylene Blue could not be used in preparing electrodes selective to anionic detergents owing to the solubility of the organic salt in the aqueous solution of the detergent, but Methyl Violet was successfully used for preparing an electrode responsive to the anionic detergent. Methylene Blue saccharate could not be used as an active material for preparing an electrode responsive to the saccharate anion because the active material gradually dissolved from the organic phase into the aqueous phase. The solubility of the active material in water is not important itself but the important factor is that the active material in the organic phase is not readily stripped from the membrane into the aqueous phase. For example, Sevron Red L hexachloroantimonate was not suitable to be applied on electrode owing to its high solubility in water but was successfully used to prepare a liquid state electrode. When the liquid state electrode was stored in $10^{-3}$ M hexachloroantimonate solution the electrode functioned satisfactorily after five weeks of preparation. There was no sign of dissolution of
dye salt in the aqueous phase from the membrane but this sign was observed when the electrode was stored in water in the absence of the relevant ion; the lifetime of the electrode in this case is much shorter. It was found also that a bromide solution having a concentration greater than $10^{-1}$ M, in the absence of mercury(II) destroyed the mercury(II) membrane electrode based on Methyl Green tribromomercuric(II). Similarly, presentation of a concentrated mercury(II) solution to the membrane before addition of the bromide buffer caused stripping of bromide ion from the membrane complex. For these reasons, it is recommended that the electrodes be stored in solutions of $10^{-3}$ M of the relevant ions. The pH of the solution has to be considered in some cases as pH adjustment aids in stabilization of the reactive form of the dye. For example, Brilliant Green which is used in part of this work, is pH dependent. It remains in the $R^+$ form between pH 4.5 and 7.0 (159). The lower pH is that at which the $R^+$ form is further protonated to the $R^+H^2$ form; the upper pH limit corresponds to the conversion of $R^+$ form to the carbinol base.

It is very important that the active material is able to equilibrate very quickly with the ion to be measured and not with any other ions forming the complex. For example, $(Ph_4As)_3Fe(SCN)_6$ and $(Ph_4As)_3In(SCN)_6$ equilibrate very quickly with SCN$^-$ and not with Fe(SCN)$_6^{3-}$ or In(SCN)$_6^{3-}$; electrodes based on these active materials did not respond to Fe(SCN)$_6^{3-}$ or In(SCN)$_6^{3-}$ but they responded to SCN$^-$. Similarly, electrodes based on $(Cu. Phen_2)$ Rose Bengal gave a steady response to Cu. Phen$_2^{2+}$ after more than 10 minutes due to the slow equilibrium between Cu. Phen$_2^{2+}$ in the aqueous solution and the
active material in the membrane. The response was non-Nernstian.

It is a general case with these liquid state electrodes that the potential (in a particular solution) drifts in one particular direction after preparation and the extent of the drift depends on the dye salt used and on the rubber. The drift is more marked when highly cross-linked natural rubber was used than when lightly cross-linked natural rubber was used. It was observed that the drift is more pronounced when the dye salt does not seem to be distributed uniformly throughout the rubber. It is believed that gradual redistribution of the dye salt throughout the rubber is one of the factors responsible for the potential drift. The drift is most marked within one day of preparation than for the following 4 weeks, in some of the electrodes. For this reason, it is recommended that the electrode be conditioned overnight in $10^{-3}$ M solutions of the relevant ion. The reproducibility, however, is good on one particular day, i.e. within 1 mV. Steady responses with these liquid type electrodes were observed within 3 minutes when it was moved from a more concentrated solution to a more dilute solution and less than 2 minutes for a move from the dilute solution to the more concentrated solution. The response time was shorter in some cases. The slope of the potential versus $-\log$ of the relevant ion concentration remained unchanged throughout the lifetime of the electrodes.

The selectivity of these electrodes is only moderate and it is difficult to assign values to the selectivity constant of these electrodes, when more than one ion forms a complex with the same basic dye; the electrodes are gradually converted to full response
to the interfering ion. It seems that most of the common ions such as Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Hg$^{2+}$, Fe$^{3+}$, In$^{3+}$, Ag$^+$, Na$^+$, K$^+$ and Cl$^-$ do not interfere seriously but ClO$_4^-$, SCN$^-$ and, to a lesser extent, NO$_3^-$ interfere in most cases. Hg$^{2+}$, Fe$^{3+}$, In$^{3+}$ and Ag$^+$ may cause serious interference when the determination is made in high concentration of hydrochloric acid or potassium bromide when they can form complexing ion such as FeCl$_4^-$, FeBr$_4^-$, HgBr$_3^-$ or AgBr$_2^-$, because these ions form ion-association complex with the basic dye. Possible interference throughout the work was studied by observing the effect of $10^{-2}$ and $10^{-3}$ M concentrations of the interfering ions on the values of the potential obtained with the electrode in contact with a $10^{-4}$ M of the primary ion. When the potential change was very small (0-2mV) at the two different concentrations of the interfering ion, this was considered as an indication of negligible interference by this ion. When the change in the potential was more than 2 mV in the positive or negative direction, the electrode was conditioned in a $10^{-3}$ M solution of the interfering ion for at least one hour and subsequently was used to observe the slope of the potential versus $-\log$ of the interfering ion concentration. The selectivity constants were calculated from these results using the equation

$$K_{\text{primary ion/interfering ion}} = \frac{E_{\text{primary ion}} - E_{\text{interfering ion}}}{2.303 \, RT/2F}$$

where the two potential readings were taken at the same concentration of the primary and interfering ion. The method is simple and was found to be reliable in most cases. It is important to notice that the interference reported in this method is only negligible at the
highest interfering ion concentration used in the study or below that but it may be pronounced at higher concentrations.

Throughout the work the potentials were listed versus the ion concentration. It is necessary to note that in some cases the salt does not exist completely in the ionic form. It is also necessary to notice that electrodes respond to the activity change and not to the ion concentration change. When the salt is in ionic form completely, the activity coefficient of the solutions can be calculated using the extended form of Debye-Huckel equation (198)

$$- \log F = \frac{A z^2 \sqrt{I}}{1 + \sqrt{I}}$$

where

- $F$ = the mean ion activity coefficient;
- $z$ = the ionic charge of the ion;
- $A = 0.5115 \text{ mol}^{-1} \text{ litre}^{1/2}$ at $25^\circ \text{C}$; and
- $I$ = the ionic strength of the solution.

When there is not complete dissociation a knowledge of association constant is necessary before calculating the activity coefficient.

Throughout the work a saturated calomel reference electrode was used as neither chloride nor potassium interfered in any of the electrodes studied. This does not eliminate the effect of changes in liquid junction potential but this can be reduced by the addition of an inert electrolyte to both test and calibration solution to bring them to a fixed ionic strength; such addition hopefully keeps the activity coefficients constant. In any case, the problem did
not exist when a fixed large amount of hydrochloric acid was added before the determination of antimony, thallium, gold, indium and iron or when a large fixed amount of potassium bromide was added before the determination of mercury, indium and iron. An Orion double junction (model 90-02) electrode was used as reference by Pathan (178). A non-leak calomel reference electrode, based on a membrane of tissue paper containing potassium chloride and covered by PVC, was used by Cooke (199).

Most of the basic dye salts which were used successfully in liquid-state membrane electrodes were found not to be suitable as active material for use in silicone rubber as PVC membrane electrodes or for applications on the selectrode. This is partly due to the solubility of these salts in water in the absence of the organic solvent but the main reason is believed to be due to the difference in the process by which the ion to be determined moves across the liquid state and solid state membrane. Eisenman (200) studied the similarities and differences between liquid and solid ion exchanger and their usefulness as ion specific electrodes. He concluded that the principal difference results from the fact that the ion exchange sites, which are spatially fixed in the solid membranes, are free to move in the liquid systems. This means that undissociated ion pairs between sites and counterions, which are immobilized in the solids, contribute to the movement of species in the liquid.

The liquid-state ion selective electrodes under discussion are inexpensive and can be readily prepared, so they can be used as substitutes for expensive commercial electrodes. The appropriate
basic dye salts are readily prepared and it is convenient to store sufficient for all subsequent use. When the basic dye salt was not prepared but was extracted directly into the organic solvent, the extraction was easy and the organic solution of the basic dye can be stored for longer periods of time for subsequent use. For example, an o-dichlorobenzene solution of Brilliant Green was used satisfactorily after one year of preparation. The membranes themselves are very readily prepared from the organic solution of the dye salts.

A considerable amount of work has been published by Russian workers (165,166) indicating the possibilities of extraction of various elements in the form of simple anions or complex anions with basic dyes. It is, therefore, suggested that further work should be carried out to investigate the large variety of basic dye ion-association complexes for use in membrane electrodes. Basic dyes which are not very pH dependent ought to be particularly useful in the further development of these electrodes. Moreover, the use of such basic dye salts may be extended to all different forms of liquid-state membrane electrodes.
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