Calixarenes and Their Application in Chemical Sensing

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by

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Declaration

I hereby declare that the contents of this thesis, except where otherwise stated, are based entirely on my own work, which was carried out in the School of Chemical Sciences, Dublin City University.

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Dr. Dermot Diamond
(supervisor)

This thesis is dedicated to my parents.

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Abstract

Potassium and caesium ion-selective electrodes (ISEs) have been fabricated from poly(vinyl chloride) matrix membranes containing nine different calixarene-based ionophores. They were used with 2-nitrophenyl octyl ether as plasticising solvent mediator. An anion exchanger [potassium tetrakis (4-chlorophenyl) borate] was included in the ISE membrane construction in some electrodes. The electrodes studied so far showed excellent response characteristics, i.e. near Nernstian response over a wide concentration range (1×10^{-4}M to 1×10^{-1}M). Selectivity coefficients were determined for nine metal cations. The best sensor had a lifetime of more than ten months and a dynamic response times was less than 9 seconds ($t_{90\%}$).

Some preliminary results on the performance of solid-state potentiometric sensors based on new materials are also included. These are based on polymeric calixarenes, which have the advantage of producing devices with the active component bonded to the substrate surface. This can simplify the manufacture of the sensors, and prevent the gradual leaking of the active component into the sample. Subsequent to this, the electrodes properties were evaluated by focusing on the stability of their potential response, selectivity, lifetime, and pH dependence.

In the final part of this research a chromogenic calix[4]arene was investigated as a lithium or sodium ion selective indicator system. Colourless solutions of the ligands in THF changed to a yellow colour upon contact with Li^+ or Na^+ ($LiCl$, $LiClO_4$ or $NaCl$ or $NaClO_4$, but not other salts) in the presence of morpholine as a base. It was found that nitrocalix[4]arene was a suitable indicating system capable of detecting lithium and sodium ions over a wide concentration range. The colour density was concentration dependent. These chromogenic compound could have important application in the fabrication of new opto-sensor for sodium and lithium.

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Chapter 1

Characterisation of

Ion-Selective Electrodes

1.1. Introduction

The analytical chemist often considers use of an ion-selective electrode (ISE) for a trace level determination of an inorganic ion[1]. This approach is advantageous because of the speed and ease of ISE procedures in which very little sample is required. Further, an ISE possesses a wide dynamic range, and is relatively cheap. These characteristics have inevitably led to the development of sensors for several ions, and the list of available electrodes has grown substantially over the past two decades. An increasing interest in the use of ISEs as chemical sensors have been reported in recent years[2]. Nowadays, commercially available ISEs for some dozen ions allow a simple and a rapid determination of the activity of inorganic ions. There are a lot of commercially available analytical instruments connected with ISEs such as sodium- and potassium-ISEs, which are generally based on glass and valinomycin, respectively. In the clinical analysis of inorganic ions, flame photometric analysis has been used, by which one can measure the concentration of an ion very accurately. However, ISEs have begun to be employed in this field recently because it is a rapid method for the analysis of inorganic ions and also because it needs no dangerous materials like high-pressure propane gas in the flame photometric analysis. Despite the fact that ISEs are very useful, but they have many disadvantages. For example, some of these sensors are complex to construct, are expensive, and a big sample solution volume may be required.

ISEs are potentiometric devices which can show a selective (but not specific) response for a particular target ion known as the primary ion. In recent times, much interest has been focussed on the use of substances known as neutral-carriers to produce ISEs, such as antibiotics, macrotetrolides and crown ether derivatives[3] in clinical chemistry and bioelectrochemistry. Calixarenes have also been used in this area, and almost two dozen patents have been issued during the last several years describing a variety of calixarenes, and claiming various applications.

1.2. Basic Theory and Properties of Ion-Selective Electrodes

1.2.1. Basic Theory

1.2.1.1. The Electrode Measuring System

Potentiometry is an electroanalytical method, based on the null current measurement of electrode potentials. The electrode response should obey the Nernst equation, which relates the logarithm of the primary ion activity to the measured potential[4,5]. ISEs may be classified, as follows:

<A> Solid-state membranes;
<B> Glass membranes;
<C> Liquid ion-exchanger membranes;
<D> Neutral-carrier liquid membranes;
<E> Special membranes.

The analytically important contribution to the overall cell-potential is generated at the phase boundary between the electrolyte and the electrode membrane. In the ideal case, the value of this potential depends on the ion activity in the sample solution. This potential is measured against a constant potential generated by a reference electrode such as the calomel electrode.

Reference electrode ISE

Hg; Hg_2Cl_2; KCl (satd.) / salt bridge / sample / membrane / internal solution; AgCl; Ag

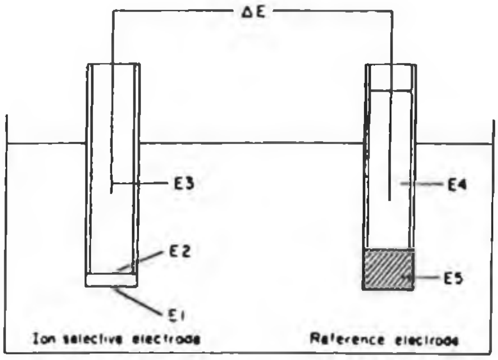

Fig 1.1. Contributions to the overall cell potential[6]

E_1------the sample / membrane boundary potential;

E_2------the membrane / internal solution boundary / potential, fixed by the solution within the electrode;

E_3------the potential of the internal reference electrode (e.g. Ag/AgCl), determined by the composition of the internal solution;

E_4------the internal potential of the reference electrode, determined by the concentration of the reference electrolyte solution (usually saturated KCl solution);

E_5------the diffusion potential at the diaphragm of the external reference electrode.

1.2.1.2. Nernstian Response

An ideal ISE should have Nernstian response over a given range of activity, with the curve of electrical motive force (EMF) versus logarithm activity being linear with a slope(S) of $2.303 \times 10^3 RT/zF$ ($59.16/z$ in mV at 25°C), where: R = gas constant; T = absolute temperature; z = charge of the primary ion; and F = Faraday constant. The slope is 59.16 mV/decade for a monovalent ion and is 29.58 mV/decade for a divalent ion at 25°C, the slope value will change with the absolute temperature. The Nernst equation is showed below:

$$E = E^0 + S \log a_i \qquad (1.1)$$

where:

E = measured cell potential;
E^0 = standard cell potential;
a_i = primary ion activity.

1.2.1.3. Activity versus Concentration

when the solute is dissolved in the sample solution, the activity is equal to the product of the concentration and an activity coefficient which depends on the concentration. If the electrolyte solution can be absolutely diluted, the ions can be considered to be completely random and the activity coefficient is unity. If the concentrations of the electrolyte solution is higher, the activity coefficient is less than one due to the attractive forces between an ion and the surrounding ionic atmosphere. The relationship between activity and concentration is given by:

$$a_i = f_i \cdot c_i \qquad (1.2)$$[7]

Where

F_i= activity coefficient of an ion species i;

a_i= the activity of i;

c_i= the concentration of i.

The activity coefficient is a function of the ionic strength of the solution, which in turn depends on the concentration of all ions present.

$$\log f_i = 0.512 z_i^2 [\, I^{0.5}/(1+I^{0.5}) - 0.2I] \qquad (1.3)^7$$

and

$$I = 0.5\, \Sigma c_i z_i^2 \qquad (1.4)^7$$

where:

I = ionic strength.

It must be emphasized that ISEs respond to the activity of the free ion in solution. ISEs provide one of the few ways of obtaining direct activity measurements of particular ionic species in solution. However, the preparation of accurate concentration standards is easy. So it is important to investigate how an ion selective electrode responds to change in concentration as well as change in activity.

1.2.1.4. Liquid Junction Potential

The boundary between the sample and the bridge electrolyte of the reference electrode leads to the generation of a liquid-junction potential. This arises from deferences in the rates of diffusion of the ionic species present in the salt bridge. This extraneous potential cannot be eliminated entirely, but it can be reduced by using a salt bridge incorporating a concentrated solution of a salt of two ions similar ionic mobility such as KCl[8].

1.2.1.5. Measurement of Selectivity Coefficients

The selectivity coefficient (K^{Pot}_{ij}) may be defined as the ratio of the primary ion concentration to the interfering ion concentration which produces the same cell potential. It reflects the ability of an ISE to distinguish between the primary ion (i) and an interfering ion (j). An ideal electrode should have a $K^{Pot}_{ij}=0$ for all interfering ions (j). There are a number of ways to calculate K^{Pot}_{ij}, the most common of which are the mixed solution method and the separate solution method:

(a) Separate solution method (SSM):

The cell potential (E_1) is measured in a solution of the primary ion (i) at activity a_i, and the process repeated in a solution of the interfering ion (j) which is present at an equal activity (a_j) to that of the primary ion (i.e. $a_i = a_j$) to give the potential (E_2). The selectivity coefficient can then be calculated according to equation 1.5[9].

$$\text{Log}K^{Pot}_{ij} = (E_2-E_1) / S + (z_i / z_j) \log a_i \qquad (1.5)$$

(b) Mixed solution method (MSM):

It is a more realistic method of determining the selectivity coefficient. The EMF of a cell made of an ISE and a reference electrode is measured in solutions which have a constant level of interfering ion a_j, and a changing activity of the primary ion a_i. The EMF is plotted against $\log a_i$. The linear portions of this curve are extrapolated, and the selectivity coefficient calculated according to the equation (1.6)[10]:

$$K^{Pot}_{ij} = [a_{i(int)}/a_j]^{z_i/z_j} \qquad (1.6)$$

where:

$a_{i(int)}$ = the activity of i at the intersection of the two linear portions of the curve.

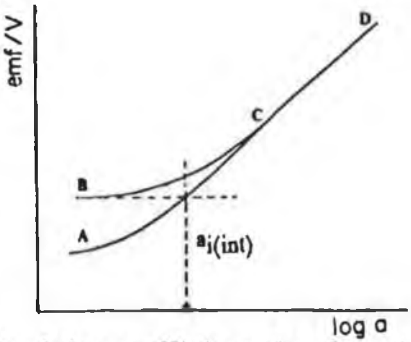

Figure 1.2. Selectivity coefficients by the mixed solution method

B-C response to (i) and (j); A-D response to (i) only

1.2.2. The Properties of Ion-Selective Electrodes

An ideal ISE should have a Nernstian response to the activity of the primary ion, and should not respond in any way to the activity of any other species present, i.e. it should be specific.

1.2.2.1. Selectivity

Selectivity coefficients are difficult to measure accurately as samples tend to be complex mixtures of many ions. As such, they should be regarded only as a rough guidance as to the likely performance of a device. It is not recommended that use of the selectivity coefficient to correct for interfering results.

1.2.2.2. Response Time

The response time of ISEs is a critical and limiting factor for many applications. It is defined as the time which elapses between the instant at which an ISE is brought into contact with the sample solution and the first instant at which the potential of the cell has reached 90% of its final value. The experimental conditions should be reported such as the stirring rate, background composition, identify of the primary ion, and the composition of the solution to which the electrode was exposed prior to this measurement. However, many other definitions (t = 50%, 90%, 95%, 99%) were adopted by workers and are still in use. A standard response time was proposed[11] which was that time required for the EMF to approach within 1 mV of its final value. However, this has been discarded since the response time values yield different results for monovalent and divalent ISEs and for activity steps of different size.

Two methods can be used to determine response time:

<A> The immersion method; In this case, the electrode is immersed in a sample of known concentration of primary ion and the transient response monitored.

<B> The injection method; This method involves injecting a small volume of a solution of the primary ion into a dilute solution which is being stirred rapidly and monitoring the response of the electrode as a function of time from the point of injection to the final steady-state potential. This was the approach used in this research.

The response times are influenced by a variety of factors including:

(a) The type of membrane; i.e. glass and solid-state membranes respond more rapidly than liquid ion-exchange membranes or gas sensing probes.

(b) The direction of concentration change; Response times are longer for high to low changes (dilution) than for equivalent changes from low to high concentrations.

(c) The volume of the test solution and the rate of stirring; Response times are shorter for changes involving small volumes with high stirring rates.

(d) The response time is increased by the presence of interfering ions.

(e) Temperature; The response time tends to decrease with increasing temperature.

Under ideal conditions, electrodes take two or three seconds to achieve a 95% response to ten-fold changes in concentration. Different experiments have quoted response times of between 15s and 30 min for large volume (about 50 cm^3) of sample contained in a beaker. Generally, about 30s or so is considered a normal response. In the presence of interfering species, or electrodes that have a history of being used with contaminated solutions, the response times can be very much greater.

1.2.2.3. The Upper Limit, Lower Limit and Limit of Detection of Measurement

The upper limit of measurement of the majority of liquid membrane electrodes is about 0.1 M. The reason is that above this concentration the membrane becomes saturated with the ion under test. The ion diffuses into the membrane and complexes with active molecules beyond the interfacial layer[12]. With concentrations below 0.1 M the ion under test complexes with the active molecules in the interfacial layer. In addition, at concentrations above 0.1 M, activity / concentration relationships become difficult to define as the fundamental equations (1.3) no longer hold.

The lower limit of measurement is generally the quantity that restricts the use of an ISE. If a solution is more concentrated than the upper limit, it is a relatively easy process to dilute it and bring it into the normal working range.

The lower limit of measurement is not the same as the lowest detection limit. Whilst an ISE may produce an EMF output in almost any solution, we need to be able to interpret the signal. Figure 1.3 shows the response of a typical ISE over a wider concentration range than previously considered.

We can see that the straight line calibration becomes curved at point A. This is the lower limit of Nernstian response and many quote this point as the lower limit for useful measurement. Whilst the calibration graph is curved below A, it can still be used for measurement. It is only when the graph becomes almost horizontal at point B

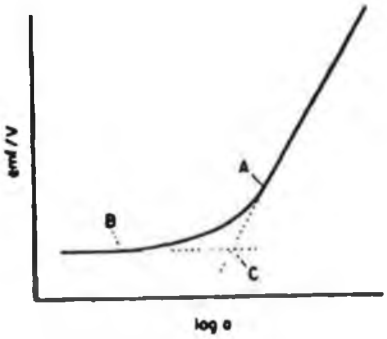

Figure 1.3 Calibration graph for a typical ion-selective electrode[12]

that measurement of ionic concentration become impossible. This is recognised in the IUPAC recommended definition of lower detection limit which states:

"The lower detection limit is the concentration of the ion under investigation at which the extrapolated linear portion of the calibration graph at extreme dilution of that ion intersects the extrapolated Nernstian portion of the graph"[12]. This is indicated by point C (Figure 1.3 above).

1.2.2.4. Stability

It is difficult to quote exact values for electrode stability as it depends upon the concentration of the solutions and level and types of interferents, and the age and storage conditions of the electrode. When working with pure solutions, electrode drift can be of the order of 1 mV per hour. The presence of interfering ions will increase this drift.

1.2.3. Ion-Selective Electrodes Based on Neutral Carriers

A large number of macrocyclic and nonmacrocyclic neutral complexing agents for cations are available, and many of them have been used as carriers in ion-selective electrode applications[13-16]. Out of about 200 carrier molecules prepared, the ligands 1, 2, 3, 4, and 5 are so far the most attractive ones[17].

1.2.3.1. Important Characteristics for Neutral Carrier Molecules

The ligands work as carriers of the metal cations in a lipophilic membrane, their most important characteristics must be[18] :

(1) Lipophilicity: the ligand and the complex must be sufficiently soluble in the membrane phase.

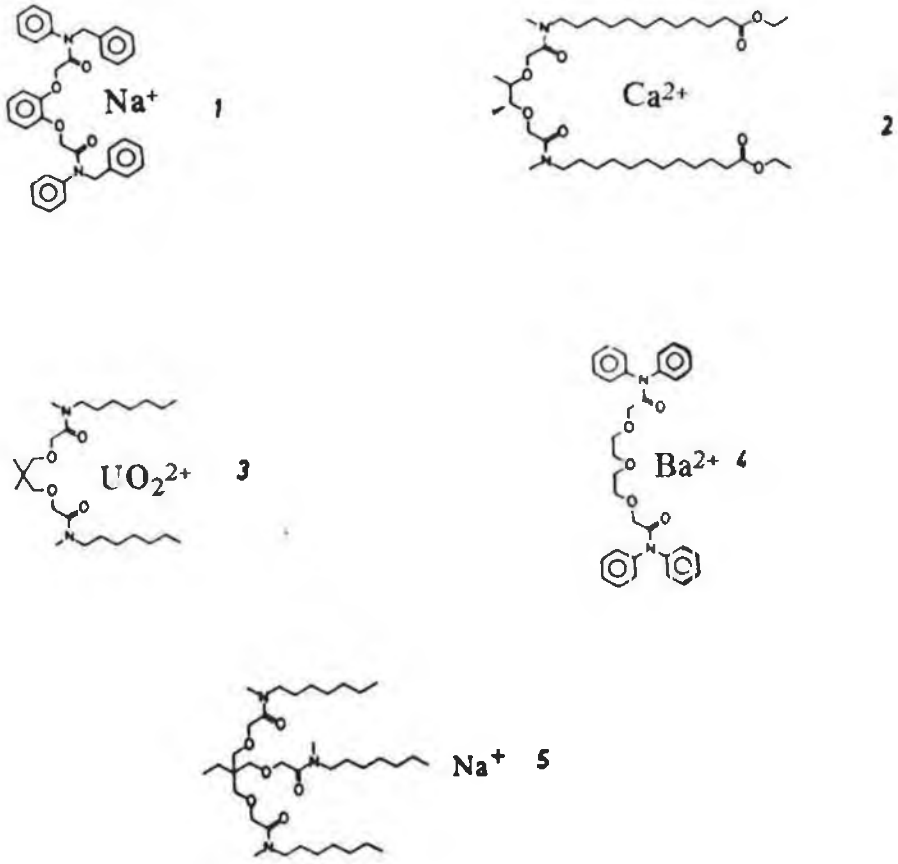

Figure 1.4. Structure of the ligands discussed

(2) Mobility: An adequate mobility of both ligand and complex are guaranteed only so long as the overall dimensions of the carrier remain within limits. But are still compatible with high lipid-solubility.

(3) Rigid polar cavity: This is required to impart Selectivity. in general, the cavity

should be of a size which ensures an optimum fit for the primary ion (see below).

(4) Kinetics: The ion exchange kinetics must be compatible with the required response time of the membrane electrode.

1.2.3.2. The Most Important Molecular Parameters for Complexing Agents

The most important molecular parameters for such a complexing agent that fulfils the requirements mentioned below are[18]:

<a> Coordination number, cavity size: The carrier molecule should be multidentate, and able to assume a stable conformation that provides optimised a cavity for the uptake of the primary ion, while nonpolar groups form a lipophilic shell around the coordination sphere.

<b> Ligand atoms: For a cation, the polar coordinating groups preferably contain carbonyl or amide oxygen atom which can provide strong ion-dipole interaction.

<c> Arrangement of the coordinating sites: These sites should preferably be arranged so as to form chelate ring with the non-solvated cation[19].

<d> Size of the ligand: A small thickness of the non-polar layer around the central atom leads to a preference for divalent cations relative to monovalent cations of the same size. This is of special importance when using polar membrane solvents.

<e> Dipole moment of the coordinating sites: Increasing the dipole moment increases the stability of the complex and the preference for divalent relative to monovalent cations of the same size.

1.2.3.3. Calixarenes

Calixarene chemistry grew from work done in the late 1960s and early 1970s in macrocyclic chemistry[20] by the 1987 Nobel Prize winners, Pedersen. Lehn, and Cram. These chemists designed and synthesized new macrocyclic ionophores which they had the ability of selectivity complexing alkali metal cations, a property which had previously been exhibited only by certain naturally occurring compounds, such as the antibiotic valinomycin used in the potassium ISE. These new synthetic ionophores were characterized by a cyclic structure with an electron-rich cavity to afford binding sites for the cation and a tailored cavity size matching the diameter of the cation to give the desired selectivity.

Calixarenes are macrocyclic phenol-formaldehyde condensation oligomers whose structures are similar to certain crown ethers and cavitands noted for their size related ion-molecule binding and phase transfer properties. The parent molecules are *p*- *t*-butylcalixarenes, i.e. the tetramer, hexamer, and octamer. In essence the calixarenes are a series of functionalised metacyclophanes with potentially convergent phenolic groups ideally suited to functional group elaboration. Calixarene derivatives containing pendant ether, amide, ketonic and ester groups have been synthesised and shown to exhibit different degrees of ionophoric activity. Calixarene or calixarene derivatives, when in the cone conformation, can form insertion compounds with small inorganic molecules which are bound in the cavities. Combination of groups with polar oxygen atoms such as ester, amide, and keton linkages with the phenolic oxygen atoms of calixarenes provides the ionophoric properties. The metal ion enters the cavity of the calixarene or calixarene derivatives, interacts with the carbonyl and phenolic oxygen atoms. Calixarene derivatives are, therefore, ideal candidates for neutral carriers for ISEs[21].

These molecules typically possess a polar cavity and a surrounding non-polar outer layer. Consequently, they are hydrophobic substances which can complex readily with ions (usually cations) by means of an ion-cavity "best-fit" mechanism when present in a non-polar membrane between two ionic solutions. They behave as ionophores or ion-carriers, spontaneously transporting ions from one solution to the other across the membrane in the direction of the potential gradient. The smaller tetrameric calixarene shows selectivity for sodium regardless of whether it is the methyl or ethyl ester[22].

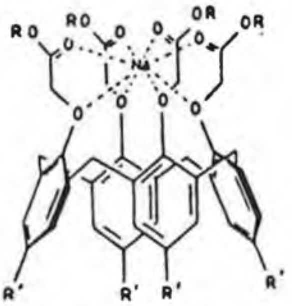

Figure 1.5 Sodium complexed calix[4]arene

The size of calixarene derivative compounds can be modified by varying the number of ring units. For the monovalent metal cation, the complexation obeys a 'best fit' principle e.g. tetramers are sensitive for sodium ions, pentamers for potassium ions, and hexamers for caesium ions. If there are other groups in the calixarene ring, e.g. oxa and dioxa calixarenes, the cavity size can be made larger[23-27].

1.2.4. Practical Methods

The basis of this technique is the plotting of a calibration graph. The samples are treated in the same way as the standards and concentration (or activity) read directly off the calibration graph. The direct reading method of analysis is quick, once a calibration graph is plotted. Recalibration is advisable, though the frequency at which it occurs depends on the electrode construction.

Under ideal conditions, where temperature, stirring, sample pretreatment etc. are carefully controlled, accuracies from +/- 1% are possible using the direct reading method. Under normal laboratory conditions from +/- 2% is a more realistic figure for monovalent ions[12], with double these figures for divalent ions. Much better precision is possible using in cremental methods such as standard additions or Gran's plot, or by potentiometric titrations.

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Chapter 2

PVC Membrane Electrodes

2.1. Introduction

Some calixarene derivatives have been shown to work well as neutral carriers for Na^+, K^+ and Cs^+ selective PVC membrane ISEs[1-5], thus reflecting the high selectivity of the calixarenes for the respective metal ions. These ISEs were based on calixarene derivatives with lipophilic aliphatic substitutents. They were found to exhibit excellent electrode properties. Further derivatives have now been synthesised and their responses as neutral carriers in PVC membrane systems are now under investigation and may produce electrodes which offer good responses as well.

2.2 Composition of PVC Membrane Electrodes

2.2.1. Polymer matrix

Some ISEs contain a polymer matrix containing the specific ingredients that impart the desired response characteristics. Poly(vinyl chloride) (PVC) is normally selected as the membrane polymer for the preparation of neutral-carrier type ISEs. A composition of approximately 50 m/m% PVC is normally adopted as lower contents of PVC result in fragile membranes, while higher PVC contents produce a substantial increase in electrical resistance and lead to sluggish responses. Also, an increase in the amount of matrix material strongly influences the diffusion coefficient of the ligand and other components in the membrane phase and may cause an increase in the rate of loss of these components from the membrane phase.

2.2.2. Solvent Mediator

The selectivity of neutral carrier ligands can be drastically influenced by the choice of the membrane solvent. An increase in the dielectric constant of a typical membrane solvent will increase the selectivity of the ligand for divalent over monovalent cations of the same size. The importance of this can be illustrated as follows: o-nitro-phenyl-n-octylether (o-NPOE), dielectric constant of approximately 24 was used as membrane solvent for Ca^{2+} and Ba^{2+} sensors[6], while a solvent of low dielectric constant, e.g. dibenzyl ether (DBE) which has a dielectric constant of approximately 4 was employed in a Na^{+} selective electrode. The effect of solvent mediators have been studied[7]. The solvent mediator in which the neutral carrier is dissolved can also function as the plasticiser for the PVC. It also has the auxiliary roles of:

1) controling the relative permitivity of the final organic phase;

2) controling the mobility of the ion exchanger sites according to the viscosity of the mediator;

3) variation in the density of the ion-exchange sites.

These auxiliary roles can enhance the partition coefficient into the aqueous phase for any particular ion, with consequent effects on electrode selectivity. A relatively high amount of solvent mediator is usually used in solvent polymeric membranes. The choice of the solvent mediator will be dictated by several criteria, such as chemical stability, chemical inertness, low vapour pressure, adequate viscosity, solubilisation properties for ligand and membrane additives, high lipophilicity, and efficient plasticising properties. These properties will in turn affect other parameters i.e. selectivity, response slope, curve linearity, membrane resistance, life time and stability. These parameters can then be optimised by the correct choice of solvent mediator. Some of the most common PVC matrix membrane electrodes are those based on the use of o-NPOE as the plasticising solvent mediator[8].

2.2.3. Ion-Exchanger

Highly lipophilic anionic sites are commonly added to conventional neutral carrier based cation-selective electrodes. The presence of permanent anionic charges tends to repel sample anions from the membrane phase, boost the cation selectivity, especially for divalent over monovalent ions by increasing the membrane polarity and they also tend to lower the membrane resistance which is desirable. Hence the incorporation of such additional anionic sites generally leads to faster response times and the dynamic behaviour is often found to become almost independent of the properties of the ionophore applied[9]. The ion-exchanger chosen for this work was potassium tetrakis (4-chlorophenyl) borate (KTpClPB).

2.3. Background to Caesium Analysis

Caesium is widely distributed in earth's crust at very low concentrations (Granites contain an average of about 1 ppm, sedimentary rocks about 4 ppm, sea water about 0.2 ppm and so on). Caesium and caesium compounds have been determined by a variety of wet-chemical and instrumental techniques including: (1) the sulphate method; (2) the chloroplatinate method; (3) the perchlorate method; (4) the sodium tetraphenylboron method; (5) the periodate method; (6) flame photometry; (7) ion-exchange; (8) neutron activation analysis; (9) emission spectroscopy; (10) x-ray emission spectroscopy[10]. Caesium as a minor constituent is determined by methods (6), (7), (8), (9), (10). Method (7) has been used to concentrate caesium-137 in milk, urine, sea water, and fresh water[11]. At present, ion-selective electrodes lend themselves nicely to the determination of alkali metal ions although no real effort has been directed towards developing electrodes for caesium. Certain crown ether compounds and a cryptahemispherand[12] have been shown to exhibit caesium complexing properties. Some hexameric calix[6]arene derivatives have shown excellent sensitivity to caesium ions and good selectivity against a range of alkali and alkaline earth metal ions[13].

2.4. Experimental Section

The objective of this research project was to design and construct potassium selective and caesium selective electrodes using a variety of neutral carrier based ionophores. The ionophores used were calixaryl derivatives which have well documented ion-complexing properties. Their performance characteristics i.e. Nernstian response, linearity, selectivity coefficients, response times and life times were assessed and the limits of detection for each ionophore was then determined.

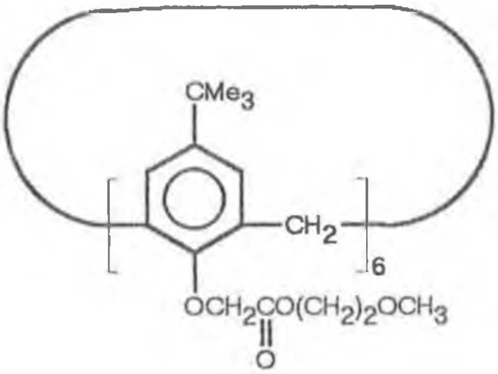
2.4.1. Calixarene Derivatives as the Neutral Carriers

The structures of the various calixarene derivatives are illustrated in Figure 2.1, namely:

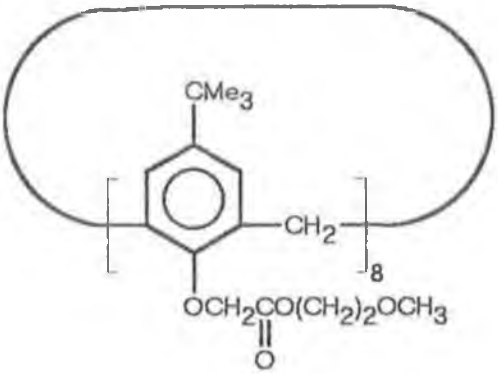
hexa methoxy ethylacetoxy -*p* - *t* -butyl calix[6]arene (ligand A);
octa methoxy ethylacetoxy -*p* - *t* -butyl calix[8]arene (ligand B);
tetra methoxy ethylacetoxy -*p* - *t* -butyl calix[4]arene (ligand C);
tetra ethylacetoxy -*p*-*t*-butyl calix[4]arene (ligand D);
tri ethylacetoxy -*p* - *t* -butyl calix[3]arene (ligand E);

p - *t* -butyloxy - *p* - *t* -butyl calix[5]arene (ligand F);
acetoxy calix[4]arene (ligand G);
hexa methylacetoxy calix[6]arene (ligand H).

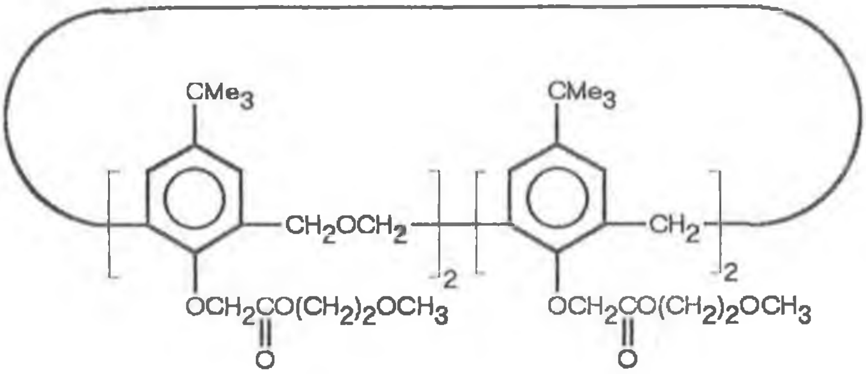
The ligands used in this study were synthesised by Dr. Stephen Harris at Dublin City University (formerly at Loctite Irl. Ltd.) and Prof. M. A. Mckervey's group at Queen's University, Belfast, Northern Ireland (formerly at University College Cork, Ireland). 2-nitrophenyl octyl ether (2-NPOE) was used as the plasticising solvent mediator and potassium tetrakis (4-chlorophenyl) borate as ion exchanger.



hexa methoxy ethylacetoxy - *p* - *t* -butyl calix[6]arene (ligand A)



octa methoxy ethylacetoxy - *p* - *t*-butyl calix[8]arene (ligand B)



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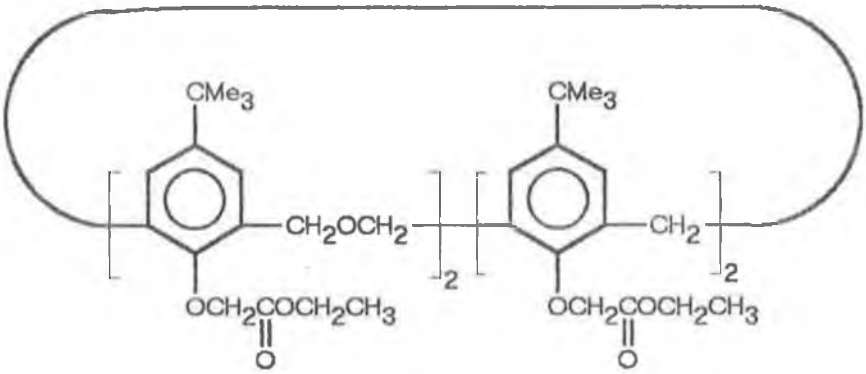

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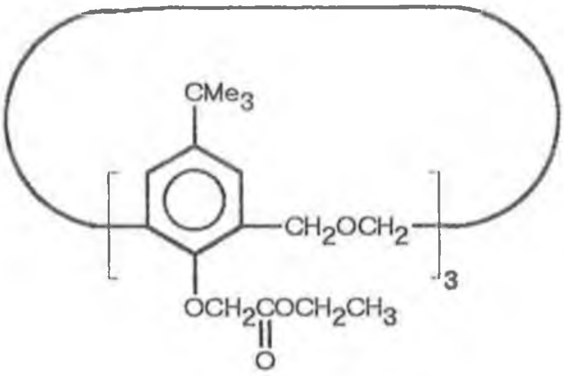
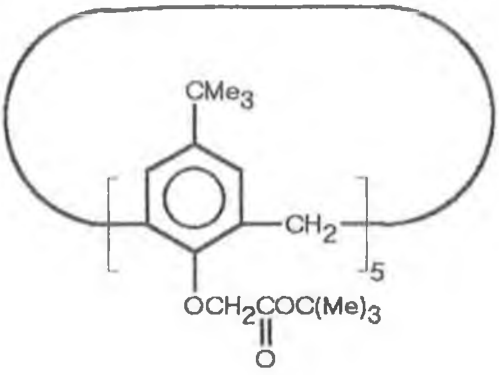
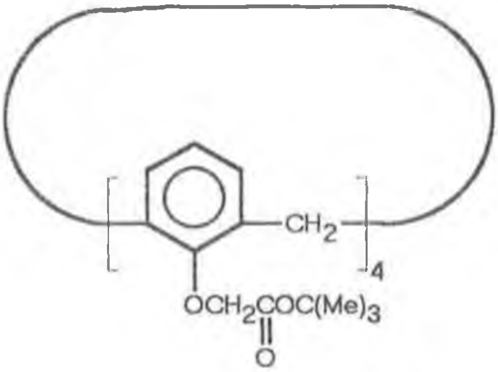


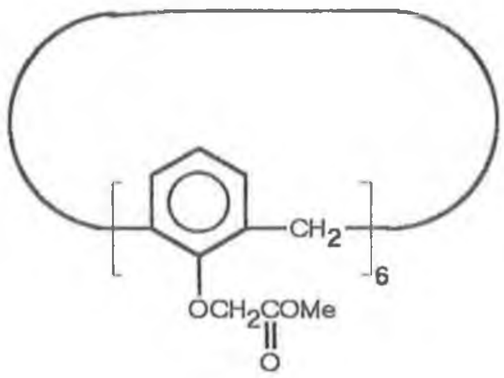
tri ethylacetoxy - *p* - *t* -butyl calix[3]arene (ligand E)



p - *t* -butyloxy - *p* - *t* -butyl calix[5]arene (ligand F)



acetoxy calix[4]arene (ligand G)



hexa methylacetoxy calix[6]arene (ligand H)

Fig.2.1 Structures of the calixarene derivatives discussed

2.4.2. Reagents and Materials

All the electrolyte solutions were prepared in ultra pure water (Millipore Grade). Analytical or reagent grade chlorides of lithium, sodium, potassium, ammonium, magnesium, calcium, rubidium, caesium and hydrogen were obtained from Reidal-de-Haen. The calibration solutions and those used to determine selectivity coefficients were made up by serial dilution. All the glassware used was acid washed in 20% nitric acid and then rinsed several times with deionised water and dried in the oven before use. The membrane materials were obtained as follows: Poly(vinyl chloride) (PVC), potassium tetrachlorophenyl borate (KTpClPB) and 2-nitrophenyl octyl ether (o-NPOE) were obtained from Fluka (Buchs, Switzerland).

2.4.3. Equipment

Electrochemical measurements were made relative to a saturated calomel reference electrode (SCE) using a Philips PW 9421 digital pH / millivoltmeter coupled to a Fluke 8060A digital multimeter to obtain 0.01 mV resolution or a universal digital pH/mV meter PT1-6 from AGB. The external reference electrode (SCE) was a Metrohm capillary tip (Ref. 6.0705.000) chosen for its stability and very low rate of KCl leakage. This ensured that errors arising from variations in junction potentials and potassium contamination of the sample were minimised. For injection experiments, the transient response time curves were observed using Philips PM 8251 single-pen recorder.

The EMF measurements were carried out on cell of the type:

Hg, Hg_2Cl_2 / KCl (satd) / sample / PVC membrane / 0.1M appropriate internal reference solution / AgCl /Ag

2.4.4. Membrane Cocktail Compositions

The membrane cocktails were prepared in accordance with the traditional procedure described by Moody and Thomas[14]. Nine PVC membrane ISEs were fabricated from various cocktails Accurately weighed amounts of each carrier (some with exchanger additive) were weighed and dissolved in the appropriate amount of plasticiser (2-NPOE). The solution was magnetically stirred on a slightly heated hotplate for approximately 20 minutes to ensure the various salts were completely dissolved and then the PVC was added. Under continuous vigorous stirring, tetrahydrofuran (THF) was added dropwise into the cocktail solution until a clear non-viscous solution was obtained. The resulting solution was allowed to settle to eliminate bubbles formed during the stirring stage. The plasticiser : PVC ratio was 2:1 m/m and the exchanger : ligand ratio was 1:10 m/m, see Table 2.1 below.

Table 2.1. Membrane cocktail compositions of Cs-electrodes and K-electrodes

(% m/m)

ISE, No.	ligand, %	plastilizer, %	PVC, %	Ion-exchanger, %
A*	A, 1.07	65.39	33.54	-
B	B, 0.61	66.29	33.03	0.07
C*	C, 1.27	65.94	32.80	-
D*	D, 0.99	66.26	32.75	-
E	E, 0.68	66.29	32.96	0.07
F	F, 0.60	66.82	32.52	0.06
G	G, 0.69	66.01	33.20	0.07
H*	H, 1.31	65.13	33.56	-
I	H, 0.51	66.57	32.87	0.05

* indicates the absence of KTpClPB in the electrode membrane.

2.4.5. Electrode Fabrication

A circular shaped glass mould was set on a large flat glass plate. A controlled amount of the prepared cocktail was poured into the mould and covered with a wad of tissue paper followed by a weight. The wad of paper allowed the THF vapour to evaporate from the mixture and prevented from particulate contamination.

Gradual evaporation at room temperature yeilded an elastic translucent membrane of about 0.1 - 0.2 mm thickness. Judith et al. found that the Nernstian response limits of electrodes decreased when the membrane thickness was increased but that increased membrane thickness also led to impairments in the lifetimes of electrodes[15]. A circular disk of about 10 mm diameter was cut out from this master membrane using a cork borer, removed gently and attached securely over the electrode cap by pressing down the outer tip. The internal filling solution was 0.1 M of the appropriate chloride primary ion e.g. 0.1M KCl. The unused PVC selective membranes were stored in air at room temperature. The electrodes were conditioned by immersion in 0.1 M primary ion solution for at least 30 minutes prior to use. When the electrode was not in use and between calibrations the electrode membranes were stored in 0.1 M primary chloride ion solution. The bench electrode body was a classical Russell gas sensing electrode (model ISE 97-7809). A chloridised silver wire was fixed to one end of the electrode body and the other end of the wire was immersed in the internal solution. The screw-on electrode tip could be removed easily and a new or different membrane clipped into place.

The fabricated ISEs and the reference (calomel) electrode were connected to the appropriate socket on the pH meter and the 'mV' option selected. The ISE was removed from the conditioning solution and washed carefully with deionised water. The calomel reference electrode was removed from the saturated KCl solution and rinsed carefully. Approximately 30ml of test solution in a 50 ml beaker was used for each measurement. The solution was discarded after use and the beaker was cleaned and dried. Generally, the most dilute solutions were measured first. However, if the electrode was to be transferred from a concentrated solution to a dilute one (e.g.10^{-1} M to 10^{-5}M), it must be washed, soaked in distiled water for 2 - 3 minutes and wiped dry before transfer.

2.5. Results and Discussion

2.5.1. Sensitivity of PVC Membrane-Electrodes Based on Calixarene Derivatives

2.5.1.1. Potential Responses

Sixteen PVC membrane electrodes based on calixarene derivatives were evaluated by determining their potential responses in pure aqueous K^+ or Cs^+ chloride solutions in the concentration range from 10^{-6} to 10^{-1}M (without ionic buffers, the range of electrode A^* was from 10^{-1} to 10^{-7}M). The lowest concentration solution was measured first. The stirring rate was kept constant at all times. The potentials was measured after an equilibration time of 1 minute. The results are summarized in Table 2.2. All potential measurements was carried out at the room temperature and the electrodes were rinsed properly between readings.

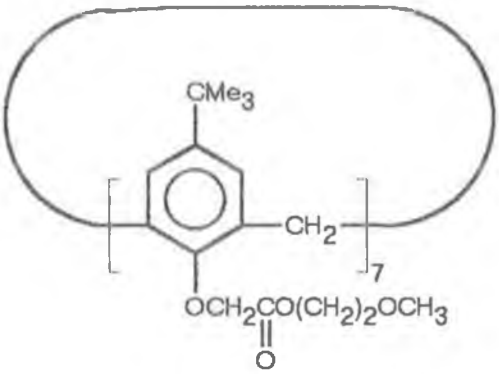
Electrode A* (ligand A), electrode B (ligand B) and electrodes H* and I (ligand H) were found to be sensitive to caesium ions. Ligands A and H contain a six-membered ringing and ligand B contains an eight membered ringing structure.

The next set of electrodes studied correspond to electrode C* (ligand C), electrode E (ligand E), electrode F (ligand F) and electrode G (ligand G) and were all found to show sensitivity to potassium ions. The ring size of these ligands varied from three membered for ligand E, to four membered for ligands C, D, and G up to five membered for ligand F.

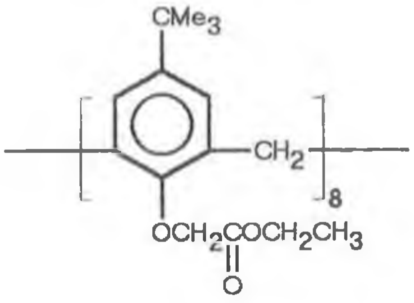
A further seven electrodes were fabricated and investigated. these contained the ligands J, K, L, M, O, P and Q (see figure 2.2). No responses to metal cations were observed for electrodes containing these ligands.

Ligand J has the same substituents as ligands A and B, but it has a different ring number, the ring number is seven for ligand J. Ligand K has the same substituents as ligand E, but they have different ring number. The ring number of ligand K is eight, and for the ligand E it is three. Ligand M is a polymer which was used to make a membrane without PVC but this attempt was unsuccessful.

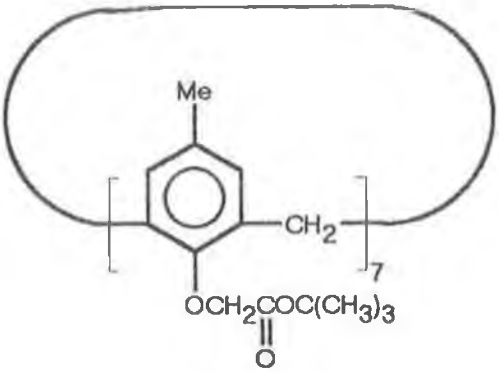
With respect to ring number and cavity sizes all the derivatives obeyed the "best fit" principle as outlined in section 1.2.3.3. Ligands containing three and four membered rings can accommodate smaller ions e.g. potassium in their cavity whereas the derivatives with larger ring sizes could accommodate the larger ions e.g. caesium.



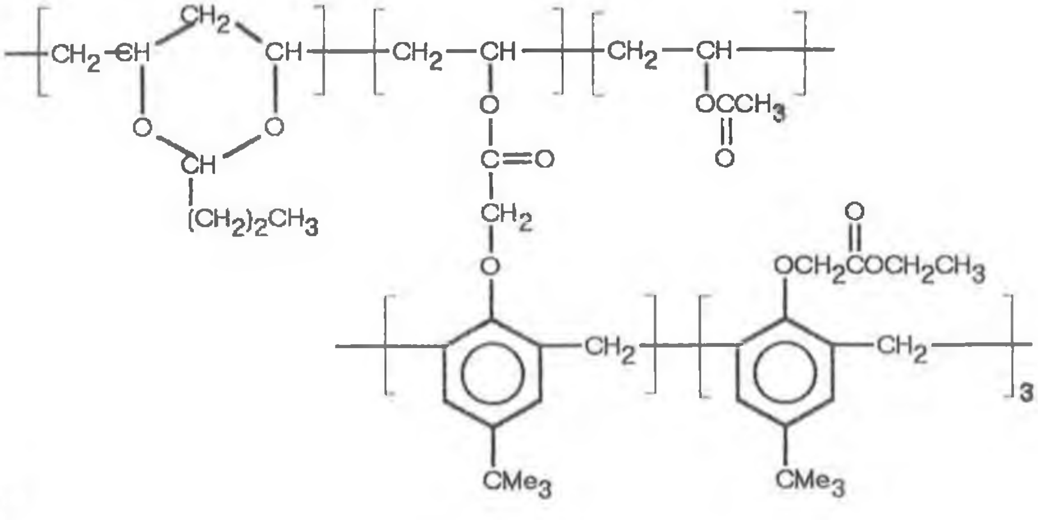
Ligand J



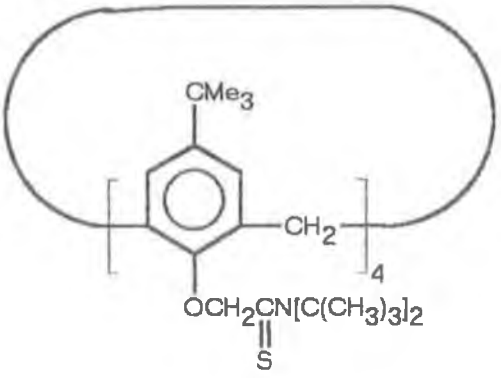
Ligand K



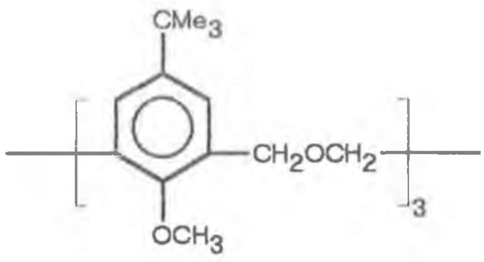
Ligand L



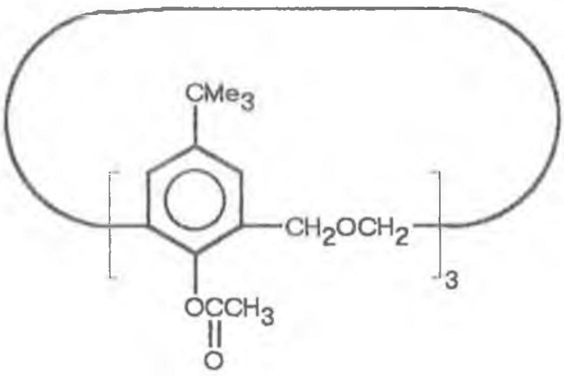
Ligand M



Ligand O



Ligand P



Ligand Q

Figure 2.2. Structures of the calixarene derivatives discussed

Table 2.2. Response in potential and function of nine electrodes based on calixarene derivatives

Concentration M	Electrode A*	Electrode B	Electrode C*	Electrode D*
$1x10^{-7}$	-179.2	-	-	-
$1x10^{-6}$	-178.4	-104.5	-141.6	-143.0
$1x10^{-5}$	-155.0	-103.6	-140.1	-141.2
$1x10^{-4}$	-104.1	-83.0	-109.2	-125.1
$1x10^{-3}$	-48.3	-49.3	-59.1	-75.4
$1x10^{-2}$	2.1	-3.1	-4.0	-20.3
$1x10^{-1}$	46.3	45.1	44.5	35.1
Resistance, MΩ	1.3	1.5	7.9	7.7
Slope, mV/dec.	52.18	50.53	53.43	55.43
Intercept, mV^{-1}	106.64	90.81	104.10	94.81
Correlation, r	0.9996	0.9961	0.9998	0.9994

(Table 2.2 continued)

Concentration M	Electrode E	Electrode F	Electrode G	Electrode H*	Electrode I
$1x10^{-6}$	-96.0	-149.4	-	-100.2	-98.2
$1x10^{-5}$	-95.3	-148.1	-41.5	-99.8	-96.4
$1x10^{-4}$	-63.0	-122.3	-48.7	-71.6	-69.4
$1x10^{-3}$	-2.1	-65.0	-2.2	-20.6	-12.3
$1x10^{-2}$	60.2	-4.1	55.1	35.2	42.1
$1x10^{-1}$	125.1	48.2	113.1	90.2	98.2
Resistance MΩ	2.8	1.1	1.1	1.2	1.5
Slope, mV/dec.	57.74	59.20	59.79	56.07	57.75
Intercept, mV^{-1}	180.30	114.89	185.03	151.01	161.61
Correlation, r	0.9925	0.9998	0.9988	0.9995	0.9999

2.5.1.2. Caesium Electrodes Response and Slope Function

The calibration curves for four caesium-electrodes A^*, B, H^* and I are shown in Figure 2.3. The ligands A and H are hexameric calix[6]arene compounds, the third ligand B is an octomeric calix[8]arene compound. The ionophores were incorporated into PVC using 2-NPOE as the solvent mediator with and without the ion-exchanger KTpClPB (see Table 2.1). In those membranes which incorporated KTpClPB, a 1:10 w/w proportion ion-exchanger : ligand was added. Electrodes A and H did not contain ion-exchanger and electrode B and I did contain ion-exchanger. From the ligand structures (Figure 2.1), it can be seen that ligands A and B have the same substituents but have different ring numbers i. e. ligand A was hexameric calix[6]arene and ligand B was an octomeric calix[8]arene. However, ligand H has the same ring number as ligand A but has different substituents at both the upper and lower ring substitution positions. All four electrodes A^*, B, H^* and I showed good sensitivity to Cs^+ ions. The responses were linear in the range 10^{-4} M to 10^{-1} M of CsCl for electrodes B, H^* and I and was 10^{-5} to 10^{-1}M for electrode A^*. Electrodes A^* and H^* based on the membranes without the ion-exchanger and electrodes B and I based on the membrane with ion-exchanger. In early work, electrodes were studied which were based on ligand A with ion-exchanger and ligand B without ion-exchanger. The results showed a non-Nerstian response. Further observation of electrodes H and I based on ligand H from Table 2.2. seemed to indicate that a real improvement in sensitivity is obtained in the membrane containing KTpClPB in comparison to those which did not contain the lipophilic anion. For example the slope was 57.75 mV/decade for electrode I, and was 56.07 mV/decade for electrode H^*. Previous work[16] has demonstrated the benefits of incorporating ion exchangers such as KTpClPB to improve the electrode response, although the ion-exchanger itself has been found to exhibit ionophoric activity towards caesium ions. The slopes of electrode I were more close to the theoretical value (the theoretical value is 59.2 mV/decade) and the slopes of electrodes A and B were 53.44 mV/decade and 50.53 mV/decade, respectively.

2.5.1.3. Potassium Electrodes Response and Slope Function

Five novel potassium electrodes were studied. They were electrodes C*, D*, E, F and G which were based on ligands C, D, E, F and G, respectively. They exhibited linear responses in the range 10^{-4} to 10^{-1} M KCl solutions (see Table 2.2 above). The slopes were 53.43, 55.43, 57.74, 59.2, 59.79 mV/decade for electrodes C*, D*, E, F and G respectively, which are all close to the theoretical value. The membranes of the electrode C* and D* were without ion-exchanger, and the electrode E, F, G were with ion-exchanger.

2.5.2. Calibration Curves and Limits of Detection

From each set of electrode results, nine response curves towards alkali metal ions were plotted with E the cell potential (mV) as the ordinate and logarithm activity (a_i) as abscissa. The plots of potential versus log a_i for certain cations are shown in Figures 2.3 and 2.4.

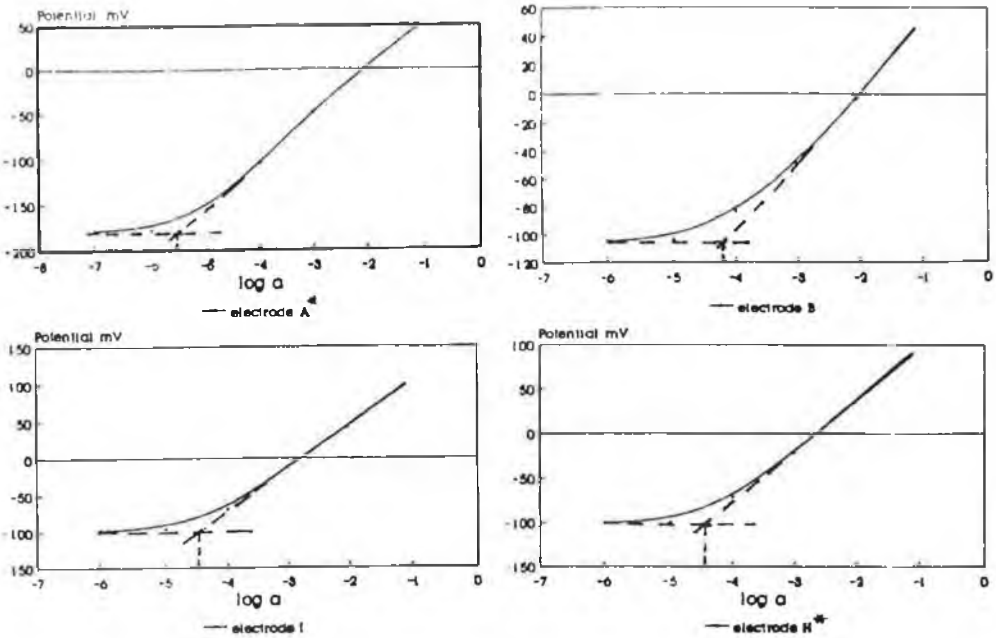


Figure 2.3. Four calibration graphs for Cs+-selective electrodes based on ligands A, B and H.corresponding to electrodes A*, B, H* and I

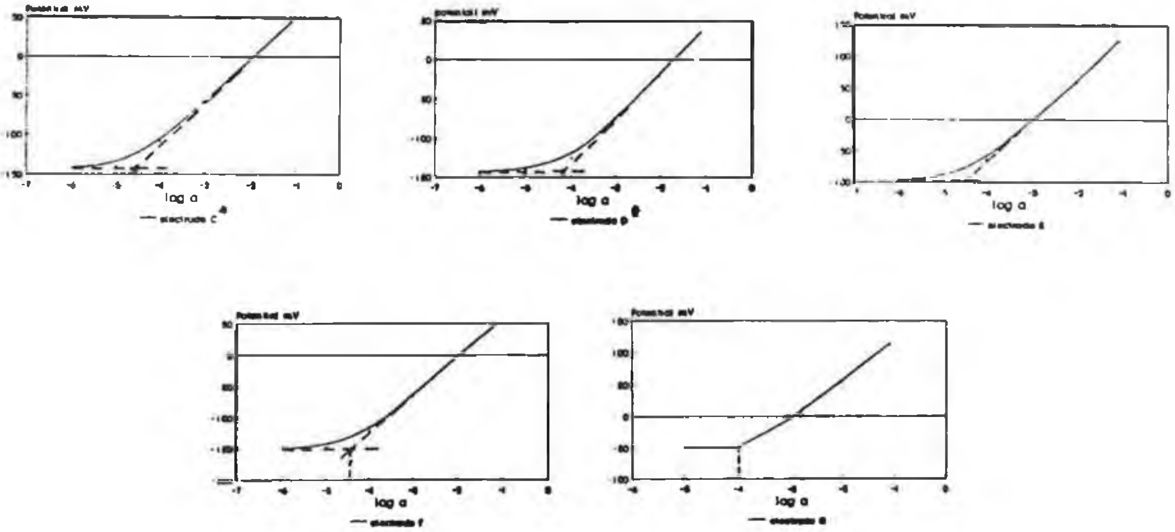


Figure 2.4 Five calibration graphs for K+-selective electrodes based on ligands C, D, E, F and G corresponding to Electrodes C*, D*, E, F and G

The limits of detection of the nine electrodes were obtained from the graphs (Figures 2.3 and 2.4) by the IUPAC method described in the section 1.2.2.3. The upper limit corresponded to highest concentration solution studied was 10^{-1}M. The limit of detection was $4x10^{-6}$ M for electrode A^*, $6.3x10^{-5}$ M for electrode B, $2.5x10^{-5}$ M electrode C^*, $5.0x10^{-5}$ M for electrode D^*, $3.2x10^{-5}$ M electrode E, $4.0x10^{-5}$ M for electrode F, $1x10^{-4}$ M for electrode G, $3.2x10^{-5}$ M for electrode H^* and $3.2x10^{-5}$ M for electrode I. Below these limits of detection there were still a response to the primary ions but the values of the slope have decreased below a Nernstian value. This part of the curve could not be used for accurate quantitative work.

2.5.3. Selectivity Coefficients

Devices based on nine calixarene derivatives were found to exhibit a Nernstian response to K^+ or Cs^+. To determine selectivity coefficients, potential measurements were made in 0.1 M solutions of interfering ions. The electrodes potential was relatively stable with drifts of not more than an average of 0.7 mV during a 3 minute reading. The separate solution method (SSM) was used to calculate the selectivity coefficients (see section 1.2.1.5). The selectivity coefficients for K^+ or Cs^+ ions against the interfering ions were calculated by applying equation (1.4) in section 1.2.1.5. The slope values used were those obtained from the linear portions of the calibration curves see Table 2.2 and Figures 2.3 and 2.4). The tabulated $\log K_{ij}^{Pot}$ values for each electrode incorporating these ligands are shown in Table 2.3. The order of preference obtained for the nine ionophors is tabulated in Table 2.4.

Table 2.3. Selectivity coefficients of electrodes (log K^{Pot}_{ij}) by the separate solution method using 0.1 M chlorides.

j =

Electrode No.	Na^+	K^+	Li^+	Cs^+	Rb^+	NH_4^+	H^+	Mg^{2+}	Ca^{2+}
A* (i=Cs^+)	-2.6	-1	-4	0	-0.8	-2.3	-2.4	-3.1	-3.2
B (i=Cs^+)	-0.9	0.4	-1.9	0	-0.6	-0.7	0.8	-1.4	-1.1
C* (i=K^+)	-1.6	0	-3.2	-0.1	-0.4	-1.2	-2.5	-2.2	-3.9
D* (i=K^+)	-1.6	0	-2.6	-0.1	-0.3	-1.1	-2.8	-2.1	-2.5
E (i=K^+)	-2.0	0		-0.4	0.1	-1.1	-3.1	-2.0	-3.3
F (i=K^+)	-0.1	0	-1.8	-0.4	-0.6	-0.9	-1.2	-1.3	-1.8
G (i=K^+)	-1.9	0	-2.3	0.01	0.3	-0.8	-2.5	-1.9	-2.9
H*(i=Cs^+)	-2.6	-1.9	-3.0	0	-0.8	-1.8	-0.8	-2.6	-2.6
I (i=Cs^+)	-2.7	-1.8	-2.9	0	-0.4	-1.8	-2.0	-2.6	-2.4

Ligands as in Figure 2.1; * indicates the absence of KTpClPB in the electrode membrane.

Table 2.4 The selectivity of the nine electrodes against the interfering ions.

Electrode No	Selectivity of the electrode against the interfering ions decreased in the following order:
A*	$Li^+ > Ca^{2+} > Mg^{2+} > Na^+ > H^+ > NH_4^+ > K^+ > Rb^+$
B	$Li^+ > Mg^{2+} > Ca^{2+} > Na^+ > NH_4^+ > K^+ > Rb^+ > H^+$
C*	$Ca^{2+} > Li^+ > H^+ > Mg^{2+} > Na^+ > NH_4^+ > Rb^+ > Cs^+$
D*	$H^+ > Li^+ > Ca^{2+} > Mg^{2+} > Na^+ > NH_4^+ > Rb^+ > Cs^+$
E	$Ca^{2+} > H^+ > Li^+ > Mg^{2+} > Na^+ > NH_4^+ > Cs^+ > Rb^+$
F	$Ca^{2+} = Li^+ > Mg^{2+} > H^+ > NH_4^+ > Rb^+ > Cs^+ > Na^+$
G	$Ca^{2+} > H^+ > Li^+ > Na^+ = Mg^{2+} > NH_4^+ > Cs^+ > Rb^+$
H*	$Li^+ > Na^+ = Mg^{2+} = Ca^{2+} > K^+ > NH_4^+ > H^+ = Rb^+$
I	$Li^+ > Na^+ > Mg^{2+} > Ca^{2+} > H^+ > K^+ = NH_4^+ > Rb^+$

Electrodes as in Table 2.1, * indicateds membrane without ion-exchanger.

According to the selectivity coefficient data for the caesium electrodes, there was a higher preference for Cs^+ ions against interfering ions with the *t*-butyl substituted and unsubstituted hexaethyl calix[6]arene ligands A and H than with the *t*-butyl substituted octaethyl calix[8]arene. This preference was, however, not enhanced by the introduction of the ion-exchanger (the selectivity coefficient values for electrode H^* and electrode I were almost same). Interestingly enough, the order of selectivity for these electrodes with respect to interfering ions was in the order $Rb^+ > K^+ > Na^+ > Li^+$.

The selectivity coefficient data of the four caesium-electrodes for rubidium ions were -0.8 for electrode A, 0.6 for electrode B, -0.8 for electrode H, and -0.4 for electrode I. Hence the strongest interfering ion for any of the caesium electrodes is rubidium. The atomic structure of caesium is most similar to the atomic structure of rubidium in these eight species of interfering ions studied. Unfortunately, electrode B showed a greater selectivity for potassium and hydrogen ions than caesium ions which was expected. Although H^+ ions can be restricted by adjustment of the pH of the solution, K^+ ions are often present as a natural constituent of many sample solutions and this would impose a limitation on the usefulness of such a caesium electrode. Electrode H^* showed very good selectivities towards Cs^+ which was also confirmed by injection experiments (see section 2.3.9.1 below).

With regard to the potassium electrodes, the results suggest that electrode F exhibited excellent selectivity against a range of alkali metal and alkaline earth metal cations with an order of preference following the sequence:

$$K^+ > Na^+ > Cs^+ > Rb^+ > Li^+$$

From the comparison with electrodes C*, D*, E and G, it can be seen that electrode F does not possesses as good a selectivity as the potassium electrodes with respect to Cs^+ and Rb^+ ions.

These excellent selectivity coefficients towards hydrogen ions can also be clearly seen in Table 2.3. The selectivity coefficient obtained for H^+ ions provided excellent results for electrode A*, C*, D*, E, G and I. Electrode E gave the best selectivity coefficient value of -3.1, while values of -2,6 -2.5, -2.8, -2.5 and -2.0 were obtained for electrodes A*, C*, D*, E, G and I respectively. The excellent selectivity of electrode H* towards hydrogen ions can also be clearly seen in the injection experiments. For the potassium electrodes, the selectivity coefficient obtained for H^+ ions provided excellent results for all five electrodes

2.5.4. Reproducibility of Electrodes

Table 2.5 Response of electrodes (mV) after the determination of the selectivity coefficients

Concentration M	Electrode A*	Electrode B	Electrode C*	Electrode D*
$1x10^{-5}$	-147	-64	-153	-156
$1x10^{-4}$	-100	-52	-106	-118
$1x10^{-3}$	-49	-16	-50	-51
$1x10^{-2}$	1	19	0.5	-7
$1x10^{-1}$	50	59	51	42
slope, mV/decade	50.8	38.1	52.8	54.4
Intercept, mV^{-1}	105.3	99.5	108.9	104.8
Correlation, r	0.9998	0.9991	0.9997	0.9965

(continued Table 2.5)

Concentration M	Electrode E	Electrode F	Electrode G	Electrode H*	Electrode I
$1x10^{-5}$	-111	-151	-85.6	-100.2	-92.4
$1x10^{-4}$	-132	-110	-55.6	-65.6	-60.4
$1x10^{-3}$	-72	-63	1.3	-14.8	-11.3
$1x10^{-2}$	-22.5	-6	60.9	40.4	43.1
$1x10^{-1}$	31	52	117.8	95.1	95.1
Slope mV/decade	55.8	56.2	53.7	55.7	54.0
Intercept, mV^{-1}	93.2	111.4	170.7	155.7	154.0
Correlation, r	0.9995	0.9982	0.9931	0.9995	0.9996

The electrodes were recalibration in standard solutions following the determination of the selectivity coefficients (see Table 2.5 above).

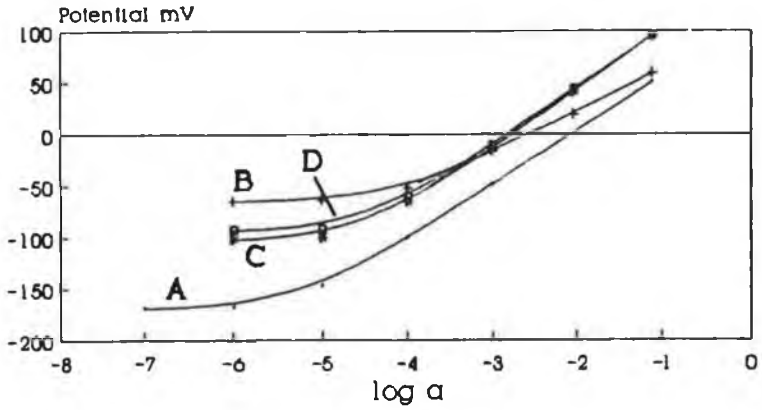


Figure 2.5 Recalibration curves of Cs-electrodes after the determination of the selectivity coefficients

curve A electrode A*; curve B electrode B; curve C electrode H*; curve D electrode I

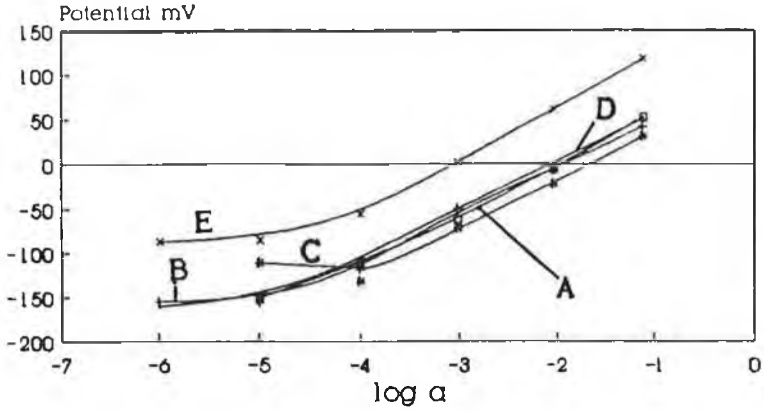


Figure 2.6 Recalibration curves of K-electrodes after the determination of the selectivity coefficients

curve A electrode C*; curve B electrode D*; curve C electrode E; curve D electrode F; curve E electrode G

The results obtained with nine electrodes are shown in Figures 2.5 and 2.6. Eight of the nine sensors showed a reproducible Nernstian responses in CsCl or KCl solutions, with a linear range from 10^{-4} to 10^{-1}M. Electrode B however showed a sub Nernstian response of approximately 40 mV/decade. Reproducibility responses of electrodes were mainly affected by chemical and mechanical interference (washing, cleaning, changing solutions). Temperature effects, reference electrode stability and their liquid junction are also key aspects to consider to avoid irreproducible results and variation in slopes.

2.5.5. Reproducibility of Cs-electrode H* based on Ligand H

The best performance shown by a caesium electrode was the one based on the ligand H. Because of its good stability and performance it was selected for more detailed investigation. It was transferred from a 10^{-3} M into a 10^{-2} M CsCl solution five times and measurements were taken every minute. The results showed a 0.2 mV (average of five measurements) reproducible response on transfer of the electrode H from a 10^{-3} to 10^{-2} M solution.

2.5.6. Lifetime

The lifetimes of ISEs are dependant not only on the membrane properties but also on the way in which the electrodes are treated and stored. The lifetime of an electrode can be important consideration for many applications. The lifetimes of nine electrodes were studied by recalibrating them periodically in standard solutions and calculating the response slope over the 10^{-1} to 10^{-4}M range for solutions of the primary ions. During this observation period the electrodes were used routinely for 5 - 10 hours per mouth and were stored in a 10^{-1} M solution of the primary ion between use. The slopes versus times plot is shown in Figure 2.7 below.

For electrodes A^*, E and I based on ligands A, E and H respectively the apparent selectivity to K^+ and Cs^+ was maintained for four, five, and five months respectively and a lifetime of up to 10 months has been confirmed for electrode H^* incorporating the ligand H. Sometimes the response would fluctuate so fresh internal solution should be put into the electrodes. This, as well as careful maintenance of the reference electrode, rectified the responses. Electrode H^* was systematically checked over a period of 10 months for response slope and linear range. The slope at the room temperature was found to be 56.5 +/-0.5mV/decade. No systematic drift of these values was observed during the lifetime of the electrode. The lifetime of electrodes C^*, D^*, F were all three months and G was two months. The lifetime of the electrode

B was only a few hours with the performance decreasing rapidly after the determination of selectivity coefficients (see table 2.5 in section 2.5.4).

With regular use, the components of the membrane will be slowly leached from the membrane into the sample solution. Conversely, the membrane solvent will be able to dissolve a small amount of water, allowing some aqueous ions to be present in the membrane. This will reduce the specificity of the membrane with time.

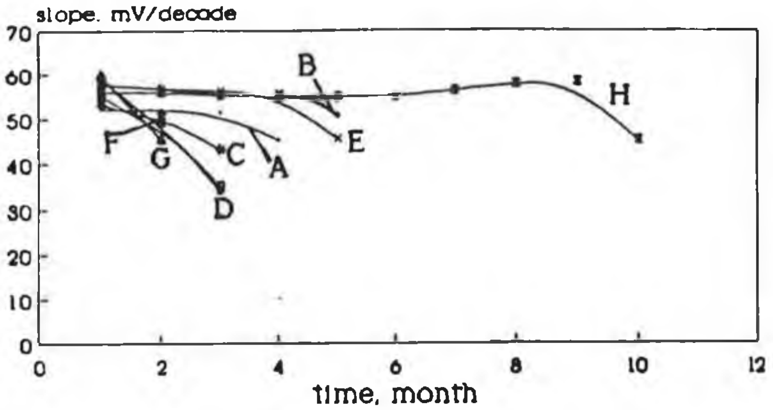


Figure 2.7 Variation of electrodes slope function with time

curve A electrode A*; curve B electrode I; curve C electrode C*; curve D electrode D*; curve E electrode E; curve F electrode F; curve G electrode G; curve H electrode H*

2.5.7. Dynamic Behaviour

2.5.7.1. Injection Experiment

Injection experiments are a crude but fast way of determining a sensor's selectivity. Of the nine electrodes studies, electrode H* was superior and was subjected to injection experiments to investigate the dynamic response and the transient behaviour of the electrode. The meter output was connected to the chart recorder input, and

100mV full-scale deflection was selected. Electrode H* and reference electrode were immersed into 20ml aliquot of a 10^{-3}M solution. A magnetic flea was used to maintain a moderately fast stirring speed. The recorder offset was adjusted to bring the signal on scale. A chart-speed of 1 mm / sec was selected. After around 10 seconds 0.18ml of 1M of CsCl solution was injected into 20ml of 10^{-3}M CsCl solution which is equivalent to a 10-fold increase in concentration for a caesium injection. Injections of 0.18ml aliquots of 0.1M solutions of various chloride cation solutions were performed in a similar manner. The results for a caesium injection for electrode H* is shown in Figure 2.8. The results for a similar injections of various interfering ion salts (Na^+, Li^+, K^+ H^+, NH_4^+, Mg^{2+}, Ca^{2+} and Rb^+) are shown in Figure 2.9. The change in potential values arising from each injection are tabulated in Table 2.5.

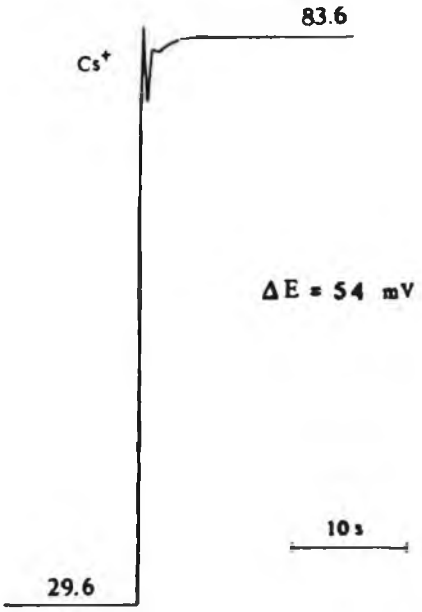


Figure 2.8 Response of electrode H* to injection of 0.225 ml of 1M CsCl solution into 20 ml of 10^{-3}M primary ion solution (theoretical response is 59.2 mV at 25°C), chart speed 1.0 mm/sec.

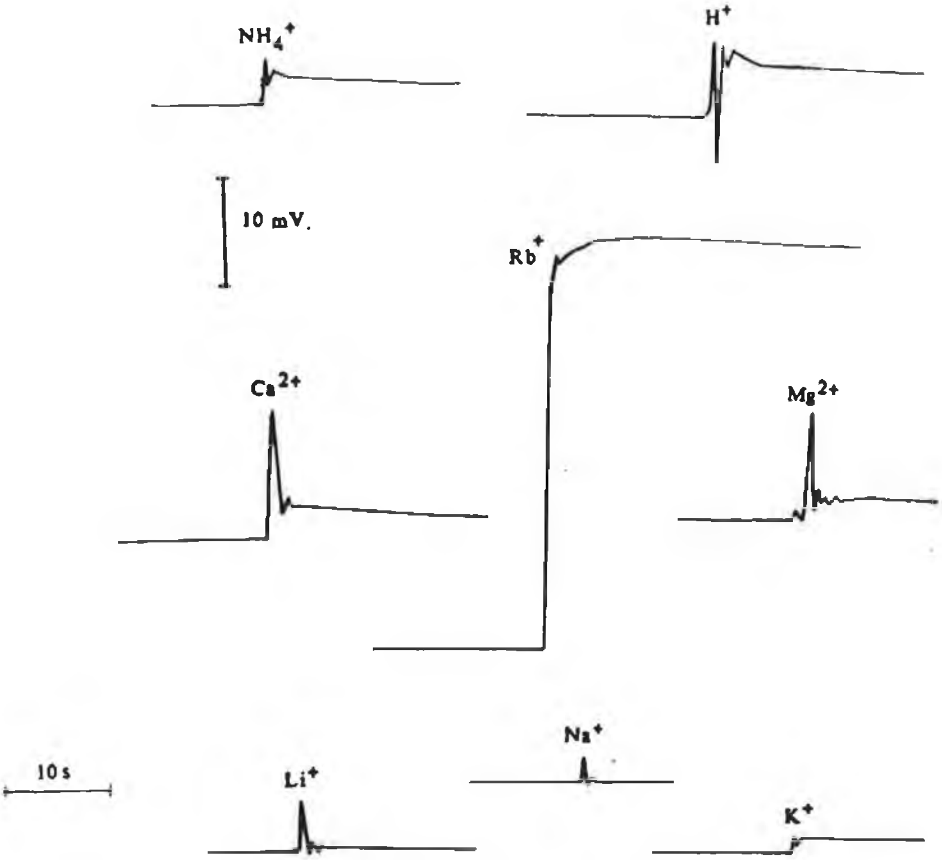


Figure 2.9 Transient response of electrode H* to 0.18 ml injections of 0.1M various cation chloride solutions into a 20 ml aliquot of CsCl.

Tab 2.6 Response of electrode H* to injections of alkali and alkaline metal ions

Ions	E_1 (before injecting)	E_2 (after injecting)	$E_2 - E_1$
Na^+	-5.9	-5.6	0.4
K^+	-18.1	-16.7	1.4
Li^+	-17.6	-17.4	0.2
NH_4^+	-20.8	-18.6	2.2
H^+	-20.4	-16.0	4.4
Rb^+	-21.5	-16.7	38.2
Ca^{2+}	-21.3	-18.9	2.4
Mg^{2+}	-21.7	-19.7	2.0
Cs^+	29.6	83.6	54.0

The dynamic response behaviour of electrode H* was obtained by recording its change in potential following a shift in concentration. The magnitude of the jump indicates the preference established by the membrane to a particular ion i.e. the selectivity of the membrane. The largest jump observed being for caesium ions followed by Rb^+ while the lowest change in potential is that observed for Li^+ Response times were fast (a few seconds) in every case. A Nernstian response was observed a 10-fold increase in CsCl solution which was completely in a few seconds (see Figure 2.8). There were very little response to the interfering cations (see Figure 2.9). Overall electrode H* showed good selectivities and a clear preference for Cs^+ cation.

2.5.7.2. Response Time

The response time was also investigated, which is a very important factor in the practical use of a ISEs based on neutral carrier. ISEs are an ideal sensor for real time measurements of primary ion changes. Further investigation of Cs-electrode H* were performed to try to assess the response time to the step-change in concentration considered above in Figure 2.8 and 2.9. They gave an indication of the fast response time. Under this injection experiment employed the response time ($t_{90\%}$) of the electrode was estimated to be less than nine seconds.

2.5.8. Interference of Hydrogen Ions

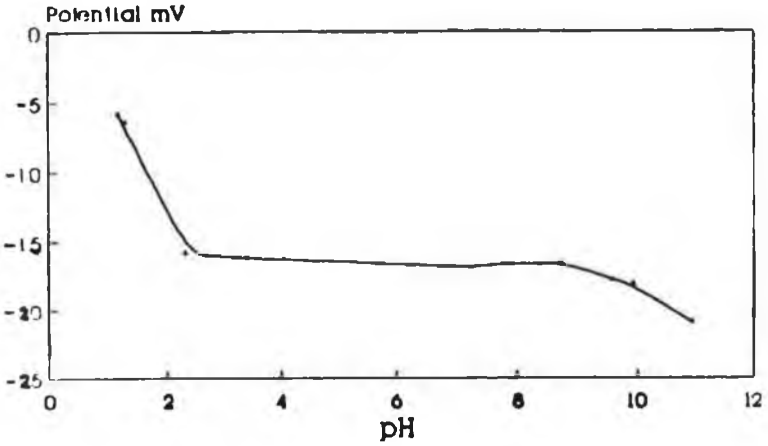


Figure 2.10 Variation of potentials with pH for electrode H*

In order to evaluate the possible interference of hydrogen ions on the potential of the electrode H, the potentials were determined by varying the pH in the following the manner:

The pH electrode, reference electrode (CE), and Cs-electrode H used were inserted into 10 ml 10^{-3} M CsCl solution. A few drops of ammonia solution (ca. 1M) was added to adjust the solution to pH 10.5. Hydrochloric acid was added dropsies to adjust to the required pH and the change in potential of the Cs-electrode could be measured simultaneously. Figure 2.10 above shows that a broad operational pH range was obtained indicating a good selectivity over hydrogen ions under these conditions for electrode H^*.

2.5.9. Determination of Unknown Solutions

The caesium-electrode H^* based on hexa methylacetoxy calix[6]arene (ligand H) was used for the determination of unknown caesium ions concentration at the room temperature. Five 25 ml standard concentration CsCl solutions (10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1} M) were used to make up calibration curve (Table 2.7. curve a below) and then the 25 ml unknown caesium chloride samples were measured. Each sample was measured five or six times repeatedly. The potentials were recorded (see Table 2.8). After that, the electrode was recalibrated (see Table 2.7. curve b). A new calibration curve (Table 2.7. curve c and Figure 2.11 curve c) was obtained by the average of a and b curves, and unknowns activities were read directly off the calibration graph c by direct reading method. The same experiment was repeated at 25°C. The calibration and recalibration curves were d and e, respectively, and average value was f. The curve c and f were showed in Figure 2.11. and 2.12, respectively.

Table 2.7. Hexa methylacetoxy calix[6]arene PVC based electrode H$^+$ response to Pure caesium solution at the room temperature

Concentration M	Calibration Curve a	Calibration Curve b	Calibration Curve c (average of curve a and b)
1x10^{-5}	-87.0	-89.9	-88.5
1x10^{-4}	-69.9	-72.8	-71.4
1x10^{-3}	-18.6	-23.1	-20.9
1x10-2	35.1	31.9	32.5
1x10^{-1}	90.6	88.8	89.7
Slope mV/decade	55.5	55.9	55.7
correlation, r	0.9995	0.9991	0.9993

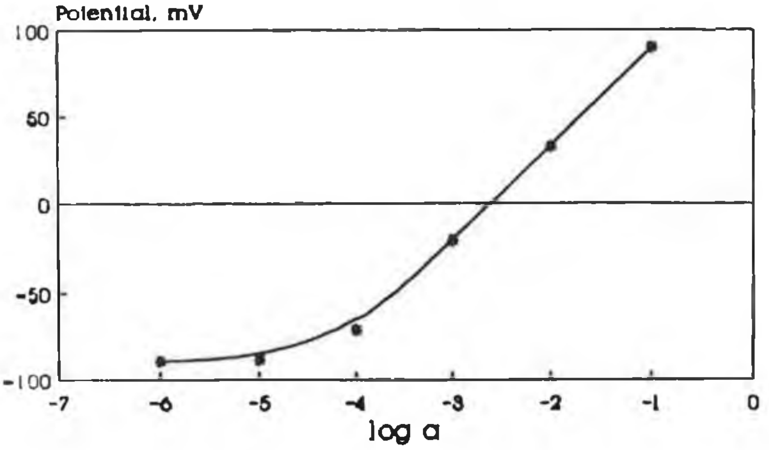


Figure 2.11. Calibration curve c (average value of curve a and b) of Cs-electrode H* based on hexa methylacetoxy calix[6]arene at the room temperature

Table 2.8. Determination of unknowns by direct reading method at the room temperature

Point	one	point	two	point	three	point	four
Potential mV	Activity 10^{-4}	Potential mV	Activity 10^{-4}	Potential mV	Activity 10^{-3}	Potential mV	Activity 10^{-3}
-60.6	1.70	-36.5	4.57	-6.3	1.60	14.5	3.78
-61.2	1.66	-36.4	4.61	-7.2	1.54	14.4	3.79
-58.0	1.89	-36.5	4.60	-7.4	1.53	15.1	3.62
-60.7	1.69	-36.1	4.68	-8.1	1.49	14.9	3.85
-59.9	1.75	-36.0	4.68	-8.0	1.49	15.0	3.86
-60.4	1.71			-7.9	1.49		
True Activity	1.97×10^{-4}		4.87×10^{-4}		1.90×10^{-3}		4.63×10^{-3}
Mean Result	1.74×10^{-4}		4.63×10^{-4}		1.53×10^{-3}		3.78×10^{-3}
Standard Deviation	8.87×10^{-6}		5.24×10^{-6}		4.32×10^{-5}		9.62×10^{-5}
Relative Standard Deviation, %	5.10		1.13		2.83		2.54
Relative Error, %	-11.7		-4.93		-19.5		-18.4

(Table 2.8 continued)

Point	five	point	six	point	seven
Potential mV	Activity 10^{-3}	Potential mV	Activity 10^{-2}	Potential mV	Activity 10^{-2}
26.5	6.21	50.7	1.69	83.5	6.55
26.5	6.21	49.9	1.63	82.9	6.39
26.9	6.31	49.6	1.60	83.4	6.52
26.3	6.16	49.7	1.62	82.3	6.23
26.2	6.13	49.1	1.59	82.6	6.30
True Activity	7.28×10^{-3}		1.74×10^{-2}		6.29×10^{-2}
Mean Result	6.22×10^{-3}		1.63×10^{-2}		6.40×10^{-2}
Standard Deviation	6.29×10^{-5}		3.77×10^{-4}		1.36×10^{-3}
Relative Standard Deviation, %	1.00		2.30		2.13
Relative Error, %	-14.5		2.30		1.75

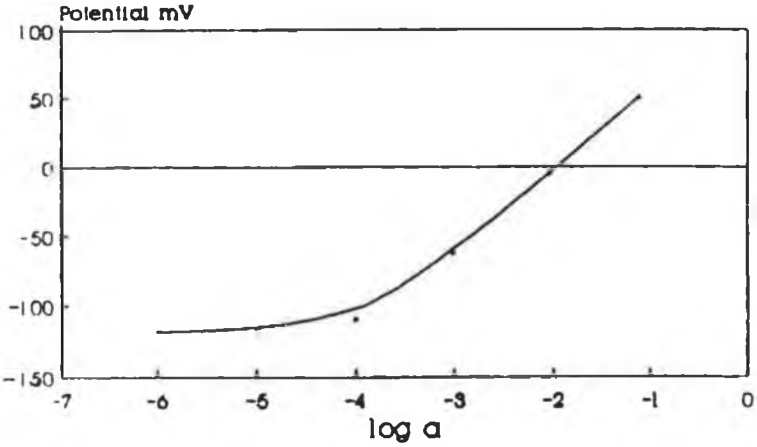


Figure 2.12 Calibration curve f (average value of curve d and e) of Cs-electrode H* based on hexa methylacetoxy calix[6]arene at 25°C

Table 2.9. Determination of unknowns by direct reading method at 25°C

Point	one	Point	two	Point	three	Point	four
Potential mV	Activity 10^{-4}	Potential mV	Activity 10^{-4}	Potential mV	Activity 10^{-3}	Potential mV	Activity 10^{-3}
-97.3	1.87	-72.5	5.23	-45.8	1.58	-23.5	4.00
-96.5	1.94	-71.6	5.43	-46.0	1.57	-23.1	4.05
-96.1	1.97	-71.0	5.57	-45.6	1.60	-23.0	4.07
-96.7	1.92	-70.8	5.62	-45.6	1.60	-23.1	4.05
-96.3	1.95	-69.9	5.83	-45.8	1,58	-23.3	4.02
		-69.5	5.93				
True Activity	1.97×10^{-4}		4.87×10^{-4}		1.90×10^{-3}		4.63×10^{-3}
Mean Result	1.93×10^{-4}		5.60×10^{-4}		1.59×10^{-3}		4.04×10^{-3}
Standard Deviation, %	3.81×10^{-6}		2.56×10^{-6}		1.22×10^{-5}		2.78×10^{-5}
Relative Standard Deviation, %	1.97		0.46		0.77		0.69
Relative Error, %	-2.03		14.99		-16.3		-12.7

(Table 2.9 continued)

Point	Five	Point	Six	Point	Seven
Potential mV	Activity 10^{-3}	Potential mV	Activity 10^{-2}	Potential mV	Activity 10^{-2}
-13.4	6.06	9.2	1.54	41.8	5.96
-13.0	6.16	9.2	1.54	42.0	6.01
-13.1	6.11	9.3	1.55	41.7	5.94
-13.2	6.11	9.4	1.56	41.6	5.91
-13.2	6.11	9.3	1.55	41.5	5.89
True Activity	7.28×10^{-3}		1.74×10^{-2}		6.29×10^{-2}
Mean Result	6.11×10^{-3}		1.55×10^{-2}		5.94×10^{-2}
Standard Deviation	5.59×10^{-5}		8.66×10^{-5}		4.66×10^{-4}
Relative Standard Deviation %	0.92		0.66		0.79
Relative Error, %	-16.1		-10.9		-5.56

According to the results of Tables 2.8 and 2.9 above, plots the graphs for the seven unknown Cs^+ concentration points, with their log activity as abscissa, and their relative error and relative standard deviation as the ordinate, at the room temperature and 25°C, respectively (see Figures 2.13 and 2.14).

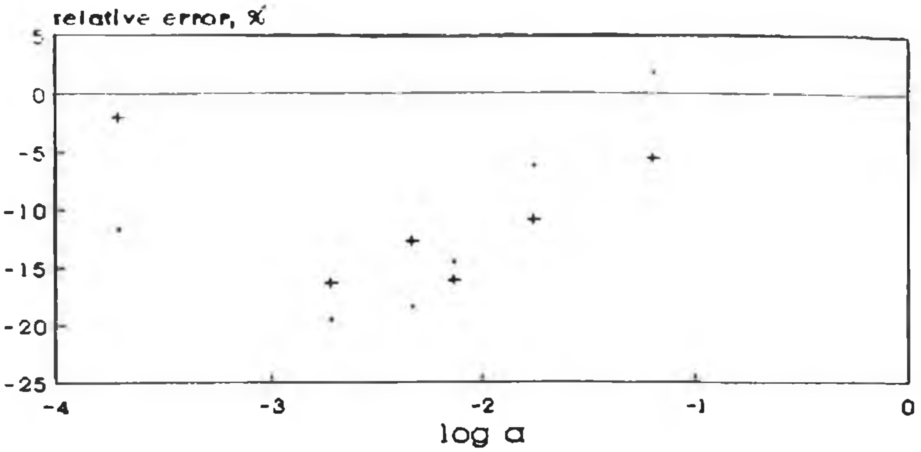


Figure 2.13. relative error versus log activity plot for caesium ion determination

· - at the room temperature; + - at 25°C

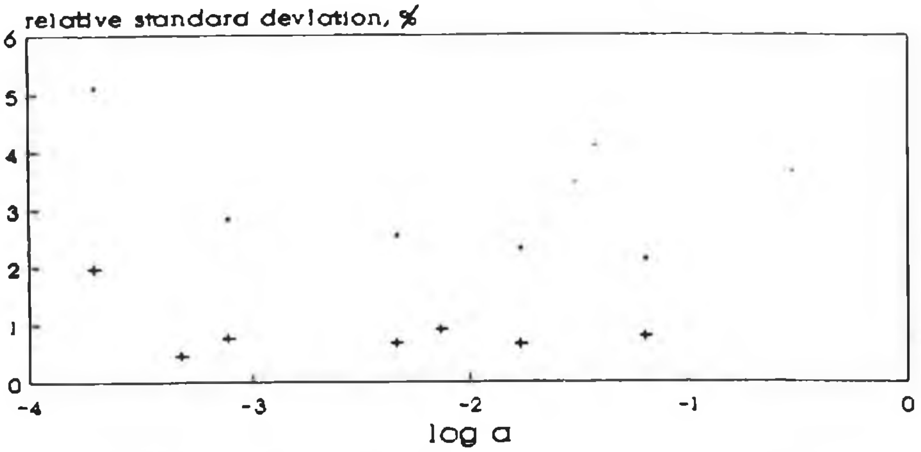


Figure 2.14. relative standard deviation versus log activity plot for caesium ion determination

· - at the room temperature; + - at 25°C

At the room temperature, the largest values were -19.5% and 5.1% for the relative error and the relative standard deviation, respectively for these seven unknown points. At 25°C, the largest values were -16.3% and 1.97% for the relative error and the relative standard deviation, respectively for these seven unknown points. The results are better at 25°C than that at the room temperature, indicating that the precisions of unknowns points less than +1.0% (see 1.3.6 direct reading method section), except for lowest activity point in the log activity versus relative standard deviation diagram. The standard deviation values were very small under both different temperatures.

The new caesium-electrode H* enables successful determination of the caesium content of sample. The results for caesium determination are of very reasonable precision, although for some individual points appeared a few errors of a few per cent. This electrode gave reproducible results and can be operated during relatively long periods of time. The error analysis suggests that:

(1) The error is concentration dependent;

(2) There is a systematic (negative) bias in the results.

These trends are commonly observed in applying ISEs to the analysis of real samples, and arise mainly from unaccuracies in the slope of the calibration curve due to faulty calibration standards, use of inappropriate regression models, electrode drift during calibration or inaccurate calibration points[17].

2.6. Conclusion

It can be concluded from the work carried out in this project that the nine calixarene derivatives synthesized were selective to K^+, and Cs^+. Nine of the seventeen electrodes tested showed excellent linearity between 10^{-1} M to 10^{-4} M (electrode A* is from 10^{-1} M to 10^{-5} M) with Nernstian slopes. Their response times were all fast (t_{90} is less than 9 seconds). They were stable and were found to work well for at least two months for eight electrodes (without electrode B). The sensors G was two months, the sensors D^*, F, C^* were three months, the sensor A^* was four months, the sensors E, I were five months. So these new K-ISEs and Cs-ISEs based on calixarene derivatives may enable successful determination of the K and Cs content of solutions, respectively. Electrode H^* based on ligand H is the best in these nine sensors. Its lifetime is ten months and response time was less than nine seconds ($t_{90\%}$). This design can be operated during relatively long periods of time in a wide pH region. Determinations with the Cs-electrode H^* read directly from the calibration curve (the procedure applied to determinate unknown sample solutions in this case) gave excellent results. The determinations were of very reasonable precision (the average values of relative standard deviation are 2.43% and 0.89% at the room temperature and 25°C, respectively) and accuracy (the average values of relative error are -9.28% and -6.94% at the room temperature and 25°C, respectively).

2.7. References

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Chapter 3

Coated wire electrodes

3.1. Introduction

There has been considerable innovation in the field of ion-selective electrodes since the invention of the glass electrode but particularly so in the last one and a half decades. Much of this work has been directed towards the way in which electrodes are constructed. The desire to miniaturize, simplify and to produce cheaper ion-selective electrodes has engrossed workers in a number of laboratories. It is not surprising, therefore, that the first report of the 'coated-wire' electrode sparked considerable interest.

Coated-wire ion-selective electrodes (CWEs) were first developed in 1971 and comprise a membrane of PVC, or other suitable polymeric matrix substrate containing a dissolved electroactive species, coated on a conducting substrate (generally a metal, although any material with conductivity substantially higher than that of the membrane can be used). Electrodes of this sort are simple, inexpensive, durable and capable of reliable response in the concentration range 10^{-1} to 10^{-4}M for a wide variety of both organic and inorganic cations and anions. The electrochemical processes occurring at the metal-membrane interface have not yet been fully elucidated. This sort of sensor, is typically only 1 - 2mm in diameter (further size reduction can be easily achieved), can be used at any angle, they cost very little to make, and they can be considered disposable, though with proper handling lifetimes of over six months have been realized. CWEs, in which the internal reference solution has been replaced by a metal contact. Sometimes exhibit better selectivities than more classical sensors with internal solution[1,2], but their standard potential is often unstable, varying for one electrode during its lifetime as well as differing between electrodes of the same type[3,4].

Since 1971 chapters in three books have been devoted specifically to coated-wire electrodes and developments and applications of coated-wire electrodes have been surveyed in several reviews and articles[5-9]. There are also a number of patents describing coated-wire electrodes[10]. One of the first advances in this area was made by Freiser et al., who developed a calcium selective coated wire electrode[11]. The electrodes were prepared by dipping the tip of metal wire in a coating solution, and allowing the resulting membrane to dry. These electrodes were based on the Ca^{2+}-didecylphosphate / dioctylphenyl phosphonate system[12]. Subsequent work has led to the development of CWEs responsive to a variety of anions and cations e.g. Ca^{2+} [13], K^+ [14,15], NO_3^- [16,17].

The work outlined in this chapter represents some preliminary results on the performance of solid-state potentiometric sensors based on new electroactive materials. The devices fabricated were based on the use of polymeric calixarene derivatives. This approach although slightly more complex than the traditional neutral carrier PVC membrane has the advantage of producing devices where the active component is bonded directly to the substrate surface. This can simplify the manufacture of the sensors and prevent the gradual leaching of the active component into the sample.

Following fabrication the electrodes were evaluated by focusing in particular on the stability of their potential response as well as their linearity, selectivity, lifetime and pH characteristics.

3.2. Theory of CWEs

3.2.1. Theory of CWEs

In coated-wire electrodes the cell configuration is:

Metal / Ion-Selective Membrane / Sample Solution / External Reference Electrode

From the thermodynamic viewpoint this is a novel arrangement which has accordingly attracted considerable critical comment. The main point at issue has been the nature of the processes operating at the wire /membrane interface in order to maintain this junction at a constant potential. Obviously, the stability of this potential must be a crucial factor in determining the utility of coated-wire electrode in potentiometric analysis. However, this is not the only factor which might cause coated-wire electrodes to show different responses from those observed with a conventional electrodes with a liquid filling using the same membrane composition. Despite the fact that the processes determining the potential across the PVC membrane layer must be the same, regardless of the electrode configuration, the asymmetry of the coated-wire leads to some significant deviations from the behaviour expected for a more traditional ion-selective electrode.

Assuming, for the present, that some mechanism does operate at the metal /membrane interface to maintain a constant internal reference potential, the overall electrode response will be determined by the combination of the membrane /sample solution boundary potential and any diffusion potential present throughout the membrane. As discussed above, diffusion potentials can arise across a membrane if an ionic concentration gradient develops. In the conventional configuration this occurs when interfering counter-ions are present in the sample solution. The membrane composition near the internal reference solution will remain constant, controlled by the composition of this reference solution. The composition of the membrane near the sample solution will reflect the extraction behaviour of interfering ions at this interface. In the case of the coated-wire electrode, since there is no internal reference solution, the equilibrium composition of the membrane will be determined solely by the composition of the sample solution and the extraction behaviour of any interfering conterions. No ionic concentration gradient will occur across the membrane and therefore there will be no diffusion potential within the membrane. Under these conditions the selectivity behaviour of the coated-wire electrode will be determined solely by the relevant distribution constants. Equation (3.1) gives the membrane potential in the coated-wire configuration for the simple case of two monovalent ions as discussed earlier for a conventional electrode[4].

$$E_M = \text{constant} + RT/F \ \text{In}(a'_A + K_d a'_B)/x \qquad (3.1)$$

where:

K_d = selectivity constant;

E_M = the membrane potential, mV.

In the coated-wire form the membrane potential is strongly influenced by the mole fraction of lipophilic ion in the membrane, x.

The polymer membranes used in ion-selective electrodes are generally relatively thick and transport through the highly viscous membrane is consequently slow. It takes many hours.

The observed selectivity of coated-wire electrodes will depend on the time allowed by experimenters for the system to reach equilibria. Even the thickness of the membrane of individual electrodes could have an influence and it might be expected that coated-wire electrodes, as a consequence would show poor reproducibility. Most importantly, since the response of coated-wire electrodes is sensitive to the mole fraction of lipophilic ion in the membrane, it is likely to show serious drift as a result of leaching of reagent. In particular, coated-wire electrodes may show poor response at low concentrations of primary ion where the limit of useful response is determined by the aqueous solubility of a lipophilic salt in the membrane. Leaching of reagent will increase the numerator and decrease the denominator in the log term in equation (3.1). As a result some coated-wire electrodes will show very high drift rate at low concentration of primary ions coupled with a reduction in useful range of the electrode.

Equation (3.1) also shows that coated-wire electrodes are likely to be affected by absorption of water from sample solutions. Many of the membranes used in ion-selective electrodes absorb water to a substantial extent. In conventional electrodes, with an aqueous internal reference solution, the water content of the membrane will remain essentially constant between measurements and the potential of the electrode is likely to be affected only by gross changes in the water activity of sample solutions. As the membrane of a coated-wire electrode absorbs water from a sample solution the mole fraction of lipophilic ion in the membrane will alter according to equation (3.1) and the potential of the electrode will drift until the membrane is saturated with water. From this viewpoint coated-wire electrodes would be expected to perform best with membranes that absorb the least amount of water. Where there is no choice of membrane available it would seem desirable to keep coated-wire electrodes moist between measurements and to pay some attention to the water activity of sample solutions.

3.2.2. The Internal Reference System in Coated-Wire Electrodes

The likely instability of the potential difference across the interface between the metal wire and the ion-selective membrane has been the focus of much critical comment on coated-wire electrodes and is one reason for their characterization as 'unlikely devices'. It is not immediately clear why this interface, which lacks an obvious means whereby electron exchange or ion exchange is facilitated, should provide a satisfactory internal reference system for the electrode. Nevertheless, the large number of reports from many different laboratories, of the successful construction and application of coated-wire electrodes indicates that they can work.

As discussed above, however, there are a number of reason why the asymmetry of the coated-wire configuration could lead to inferior performance and it is not reasonable to describe these observations solely to the lack of a defined internal reference potential. The fact that coated-wire electrodes work at all implies that some process, or processes, must operate, at least in the short term, to maintain a constant potential at the metal wire /membrane interface.

There have been several attempts to devise a model for the metal /polymer interface to explain the degree of stability which is inferred for the reference potential. Since PVC is permeable to both oxygen and water it was suggested that an oxygen electrode is set up at the platinum / PVC interface. Hulanicki and Trojanowicz[18], improved in the stability of calcium-selective electrodes using silver or graphite contacts to the membrane. They also reported improved stability for electrodes on a silver substrate in aerated calcium solutions compared with electrodes in calcium solutions that had been deaerated with argon. This evidence is consistent with an involvement of oxygen in the potential determining processes at the silver surface although it should be noted that the potential observed in deaerated solution reached the same value as that in aerated solutions after about two hours. Schindler and co-workers, observed dependence of the potential of valinomycin and calcium neutral carrier electrodes on the oxygen partial pressure above the test solution and showed that the electrode potential shifted markedly more negative when oxygen was replaced by hydrogen. They concluded that a Pt / O_2 system existed in these coated-wire type ion-selective electrodes. However the oxygen electrode is notoriously irreversible, even in aqueous solution, and R. W. Cattrall felt it is unlikely that such an illpoised system could explain the stability of potential at the platinum / polymer interface.

In summary, there are many processes which in principle are capable of explaining the relatively stable potentials at the metal / membrane interface implied by the successful construction and application of coated-wire electrodes. There is experimental evidence available from a number of sources which supports the involvement of all of these processes in different coated-wire electrode systems. Certainly, there is no single mechanism responsible for the maintenance of a stable internal reference potential in coated-wire electrodes, the potential observed being the result of a complex interaction of a substantial number of factors. Conscious attempts in laboratory to improve the performance of the internal reference system have not been particularly successful, but this is not surprising given a tendency of this configuration to emphasize the influence of some of the less favourable characteristics (d=0.4mm) was covered with a PVC membrane using n-nitrophenyl octylether as the plasticizer and a small quantity of crown ether as the ionophore. The electrodes showed high selectivity but low potential stability.

A new way of obtaining CWEs by electrolytic covering of platinum wire with chalogenides has been suggested. Thus, for example, an electrode based on a copper selenide selective to Cu^{2+} ions in the presence of considerable excess of Cd^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+} and Co^{2+} ions was made. The electrode showed potential drift of 25mV during 135 days. It is too early yet to estimate its advantages though the idea per se is interesting.

Freiser and co-workers[32] have examined CWEs responsive to anions (ClO_4^-, Cl^-, Br^- CNS^-, NO_3^-) with membranes based on PVC solutions in cyclohexanone containing the appropriate quaternary ammonium salt. The authors note that in many cases CWE selectivity is higher than that of ISEs with a liquid filling but the potential stability is low.

Srianujata and co-workers offered an explanation for the stabilization mechanism of CWE potentials[33]. The authors used CWEs made of chlorinated silver covered by a membrane (PVC DOP) for metal ion determination. Prepared electrodes were soaked for 12 hours in 0.1 M potassium chloride. According to the authors' opinion, the membrane contact with Ag / AgCl was through a thin membrane of salt water (KCl) solution rather than directly. The film appears on the metal-silver membrane boundary as the result of water and electrolyte diffusion through the membrane. Thus, a half-cell of the following type is formed.

Ag / AgCl, KCl / Membrane / Solution

Nevertheless, electrode stability is not high enough during use without frequent calibrations.

Freiser gives emphasis to the choice of plasticizer for the PVC-membrane in CWEs. A plasticizer must give a glass transition temperature for the polymer which is lower than room temperature. The role of plasticizer is especially important for CWEs based on membrane-active neutral carrier complexing agents. In this case, Freiser recommends dodecylphthalate as the plasticizer.

A critical consideration of the CWE functioning mechanism is given in Buck's work[34]. According to him, as a rule, there is no ground to expect potentials in CWEs to be stable in time. In CWEs one membrane surface comes into contact with the solution, the other with the metal wire:

$$L^+ / \text{Membrane} / M$$

where L^+ is the ion in solution and M is metal. The instability of the boundary potential is connected with the fact that reversible transition from ionic conduction of the membrane to the electronic one of the metal is not provided. Buck classified CWEs as 'completely blocked systems'. He described the ion-selective membrane-metal interface as a condenser, the conduction of which is determined by a capacity component. As there is no electrochemical equilibrium on the membrane / M interface, it must be sensitive to specific and nonspecific portion of ions and solvent molecules. All these facts cause time instability of potential and its dependence on electrode 'history'.

Thus, direct membrane contact with the electronic conductor in the majority of CWEs causes a considerable potential drift. Nevertheless, electrodes of the CWE type are of great interest due to their simplicity, ease of product ion and small size which is so important for their application in biology and medicine. These electrodes are widely used[35,36], in particular, for potentiometric titration. It seems possible that further improvement by way of creating conditions for reversible transition from electronic conduction mechanism to the ionic one will promote CWEs with a proper stable potential.

3.3. Experimental Section

3.3.1. Chemicals

All reagents used in this study were of analytical reagent grade. Standard sodium and potassium chloride solutions were prepared from a standard stock solution (1M) by serial dilution. Both calixarene derivatives shown in Figures 3.1. and 3.2. below were synthesized in accordance with methods described elsewhere[37]. The plasticizer used was o-nitrophenyl octyl ether (NPOE), the ion-exchanger was KTpClPB. Selectophore grade (Fluka) tetrahydrofuran (THF) was used as the membrane solvent and also to clean the electrode substrate prior to membrane deposition. Deionized Milli Q grade water was used throughout.

The Titanium wire was 99,99 w/w % pure and 0.127 mm diameter was used as a substrate. Silver Epoxy conductive adhesive (R. S. Components Ltd.) and solder were also used in the sensor fabrication.

3.3.2. Equipment

Electrical connections to the titanium wire were made using silver / epoxy conductive adhesive. Shielded copper wire (coaxial cable) was used as the electrode connector lead. The electrode output was monitored with a WTW pH 522 Precision pH/mV meter using the millivolt range. All potential measurements were made with respect to a Metrohm capillary tip (Ref. 6.0705.000) SCE reference electrode. Electrode membranes and structures were cured in a Memmert laboratory drying oven (type U40). Initial membrane resistances were checked using Fluke multimeters 8024B. A Philips PM 8251 single-pen recorder was used to measure the drift and response time traces.

3.3.3. Silylated Calixarene Compounds

Both calixarene silylated compounds are shown in Figures 3.1 and 3.2 identified as N and S, respectively. They were obtained from Loctite (Ireland) limited and used as received.

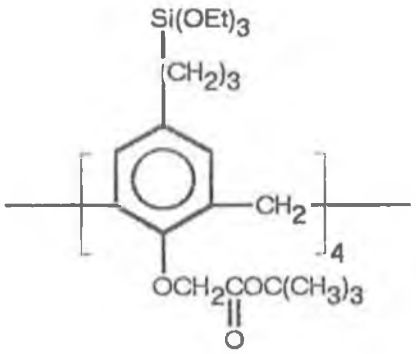


Figure 3.1. Structure of the calix[4]arene (ligand N)

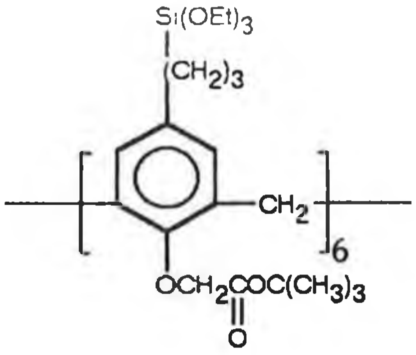


Figure 3.2. Structure of the calix[6]arene (ligand S)

3.3.4. Construction of CWEs

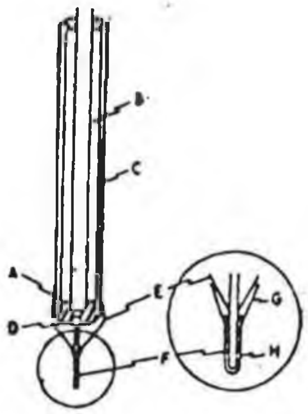


Figure 3.3. Construction of coated wire electrode
(A) epoxy resin; (B) shielded cable; (C) 8mm o.d. glass tube; (D) solder; (E) seal tape; (F) Ti wire; (G) cyanoacrylate resin; (H) membrane.

Figure 3.3 shows a schematic diagram of the coated wire electrode construction. A Ti wire was carefully soldered to a shielded cable, which formed an extension of the inner conductor of a length of coaxial cable, and positioned inside the tube and protruded into the epoxy resin while the material was still fresh. Then it was incorporated with epoxy resin in a 8 mm o.d. glass tube. The tube assembly was left to harden the epoxy resin, the junction was covered with sealing tape in order to prevent its being wetted by the sample solution. The exposed Ti wire (5 mm) was polished with sand paper, carefully washed with distiled water, then with THF and left to dry. Finally, the cable was sealed to the other and with epoxy resin.

3.3.5. Composition of Ion-Selective Membrane and Preparation

The coating solution was prepared by dissolving an appropriate amount of ligand, ion-exchanger (KTpClPB) or plasticizer (o-NPOE) with THF, as shown in Table 3.1. The optimal content of both calixarene ionophores to the total weight of the coating solution is about 99.9wt% for a Na-membrane and 97.51wt% for a K-membrane, which were found in several experiments by varying the mixing ratio of the components. In the following section both coated-wire electrodes were fabricated with this optimized composition.

Table 3.1. Optimum composition of CWEs

membrane No.	ligand wt%	o-NPOE wt%	Ion-Exchanger wt%
sodium ligand N	99.9	-	0.1
potassium ligand S	97.51	2.36	0.13

The appropriate calixarene ionophore was weighed into a 2 ml sample bottle together with the appropriate amounts of KTpClPB and o-NPOE (for the K-CWE). The mixture was slightly heated and stirred over a hot magnetic plate for up to 20 minutes. THF was added dropwise until the mixture was completely transparent. The resulting solution then underwent controlled evaporation of the THF until a 'runny-honey' type consistency of the membrane cocktail remained.

3.3.6. Preparation of Electrodes

The general method for making coated-wire electrodes is given below. The prepared bare CWEs were dipped into a constant depth into the coating solution approximately 6 times. The solvent THF was allowed to evaporate and the calixarene derivatives were cured onto Ti wire in a oven at 140°C for Na-CWE, 130°C K-CWE. The temperature was raised slowly to prevent the cured membrane from breaking. The drying period of at least 3 hours was allowed between the dipping cycles. Ti wires were coated by dipping and drying until a small bead completely encapsulated their ends. The bead was examined under the microscope to check for cracks before use. The fabricated CWEs were conditioned for at least for 3 hours in the primary ions solution (0.1M) NaCl or KCl before use. The membrane resistance generally indicated a resistance in the region of 1 to 3 MΩ in a conducting electrolyte solution of 10^{-1}M primary ion.

3.4. Results and Discussion

3.4.1. Making Successful Coated-Wire Electrodes

Making coated-wire electrodes is said to be more of an art than a science and the following procedure seems to yield most success:

(1) Sandpaper was used to polish the exposed Ti wire to improve adherence. The exposed metal was then washed with THF, rinsed well and allowed to air dry;

(2) The junction of the coated region and taped area was also covered with the resin so as to keep the exposure length of the coated region constant. It was important to wrap the exposed part of the Ti wire tightly with parafilm;

(3) During coating the wire should be kept in a vertical position to a symmetrical and uniform layer. The wire was coated by quickly dipping (0.5-1cm) into the coating solution;

(4) A bead about 2 mm in diameter is obtained on the tip of the wire. The number of times the dipped procedure needs to be carried out will depend on the concentration of the coating mixture. The coating should be free of bubbles;

(5) It is useful to examine the bead under a microscope for holes and to check for entrapped air bubbles and membrane defects. Also it is useful to measure the resistance of the electrode since very low resistances indicate exposure of bare metal to the solution;

(6) When using the electrode it is advisable to immerse only the exposed section of the bead. Also when transferring the electrode from one solution to another, blot dry with tissue, and if rinsing of the electrode is required, this should be done preferably with a rinsing solution of the same ionic strength as the test solution.

(7) All measurements of emf were made at room temperature under constant conditions, i.e. stirring at a constant rate and the electrodes were immersed to the same depth in each solution.

(8) Care must be taken to prevent contact of the sample with bare metal. Care must also be taken when wrapping the electrode with parafilm to avoid squeezing the often quite soft bead thus loosening the bond with the metal surface.

3.4.2. Silylated Calix[n]arenes (n=4,6) as Neutral Carriers for CWEs

The calix[4,6]arenes examined are of the 4-arene and 6-arene types, they are a silylated variety. They can be polymerized onto solid metallic, substrates[37] at 140°C and 130°C, respectively. Both these compounds were identified as being suitable for direct chemical reaction with the electrode substrate surface as they are of a class of compounds known as a silane coupling agent. They react with the substrate surface via native hydroxyl sites to form silicon / oxygen / substrate bridges between the calixarene moieties and the surface (see Figure 3.4).

The CWE based on calix[4]arene silyiated compound (ligand N) has also been investigated[37] using Aluminium wire as metal substrate but the results were not as good as those obtained using the a Ti substrate.Both Ti and Al are known to bond particularly well to silylated compounds of this type.

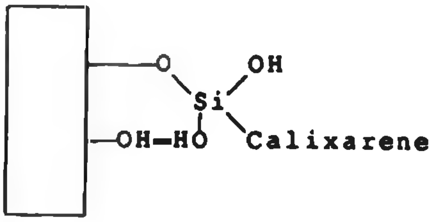


Figure 3.4. Surface of metal coupling with calixarene

3.4.3. Electrode Response and Potential Stability

A considerable drift amounting at least a few millivolts per hour was observed once both electrodes were placed in $5x10^{-4}$ M NaCl or KCl solutions. Consequently, the measurements were taken only after 2 minutes when the potential had became acceptably stable. The determinations were performed on a series of solutions of the appropriate chloride cations, the most dilute solution was measured first. Tables 3.2 and 3.3 illustrate the variation of the measured potential with time following the concentration changes for Na-CWE and K-CWE, respectively. Each series was determined three times individually over a 3 hour period for each electrode.

Table 3.2. Electrode response for Na-CWE based on ligand N

Series 1:

Concentration M	Potential mV	Potential mV	Potential mV	Potential mV	Potential mV	Average mV
$5x10^{-4}$	-84.4	-83.3	-83.4	-82.2	-81.2	-82.9
$1x10^{-3}$	-80.3	-76.0	72.4	-70.4	-68.1	-73.4
$5x10^{-3}$	-39.0	-38.3	-37.3	-36.3	-35.5	-37.3
$1x10^{-2}$	-22.9	-22.0	-21.5	-21.1	-20.5	-21.6
$5x10^{-2}$	13.9	13.7	13.4	13.2	13.0	13.4
$1x10^{-1}$	26.7	26.6	26.6	26.8	26.7	26.7
Time, min	1	1.5	2	2.5	3	

The average slope was 52.9 mV/decade, the correlatrion was 0.9999 from 10^{-3} to 10^{-1}M of NaCl.

Series 2:

Concentration M	Potential mV	Potential mV	Potential mV	Potential mV	Potential mV	Average mV
$5x10^{-4}$	-68.3	-66.7	-65.3	-64.6	-65.2	-66.0
$1x10^{-3}$	-57.5	-57.3	-53.5	-54.0	-52.7	-55.0
$5x10^{-3}$	-21.7	-22.1	-22.0	-22.0	-22.1	-22.0
$1x10^{-2}$	1.0	-0.1	-0.8	-1.3	-1.9	-0.6
$5x10^{-2}$	33.9	33.0	32.2	31.5	31.0	32.3
$1x10^{-1}$	45.2	44.5	43.8	43.1	42.5	43.8
Time, min	1	1.5	2	2.5	3	

The average slope was 52.9 mV/decade, and the correlation was 0.9982 from 10^{-3} to 10^{-1}M of NaCl.

Series 3:

Concentration M	Potential mV	Potential mV	Potential mV	Potential mV	Potential mV	Average mV
$5x10^{-4}$	39.5	38.5	37.6	36.8	35.9	37.7
$1x10^{-3}$	31.1	30.5	29.8	29.2	28.8	29.9
$5x10^{-3}$	58.4	56.8	55.0	54.0	53.0	55.4
$1x10^{-2}$	83.2	81.3	79.5	78.0	76.8	79.8
$5x10^{-2}$	107.4	105.8	104.2	102.5	101.1	104.2
$1x10^{-1}$	116.0	116.0	114.6	112.3	111.3	114.0
Time,min	1	1.5	2	2.5	3	

The average slope was 49.2 mV/decade, and the correlation was 0.9758.

Table 3.3. Electrode response of K-CWE based on ligand S

Series 1:

Concentratio nM	Potential mV	Potential mV	Potential mV	Potential mV	Potential mV	Average mV
$5x10^{-4}$	20.7	21.5	22.4	23.1	24.5	22.4
$1x10^{-3}$	15.9	16.7	17.6	18.3	19.1	17.5
$5x10^{-3}$	55.1	55.2	55.1	58.4	58.2	56.4
$1x10^{-2}$	75.1	75.5	75.5	75.4	75.3	75.4
$5x10^{-2}$	111.4	112.4	112.7	112.4	112.3	112.2
$1x10^{-1}$	126.4	126.6	126.5	126.2	126.0	126.3
Time,min	1	1.5	2	2.5	3	

The average slope was 57.6 mV/decade, and the correlation was 0.9997 from 10^{-3} to 10^{-1}M of KCl.

Series 2:

Concentration M	Potential mV	Potential mV	Potential mV	Potential mV	Potential mV	Average mV
$5x10^{-4}$	67.0	65.2	63.7	62.4	60.4	63.7
$1x10^{-3}$	69.0	67.3	65.4	64.1	62.9	65.7
$5x10^{-3}$	97.3	96.3	95.7	95.1	94.8	95.8
$1x10^{-2}$	113.0	111.9	112.7	112.2	113.4	112.6
$5x10^{-1}$	147.7	147.5	147.2	146.8	146.3	147.1
$1x10^{-1}$	159.4	160.2	160.3	160.3	160.2	160.1
Time,min	1	1.5	2	2.5	3	

The average slope was 50.4 mV/decade, and the correlation was 0.9991 from 10^{-3} to 10^{-1}M of KCl.

Series 3:

Concentration M	Potential mV	Potential mV	Potential mV	Potential mV	Potential mV	Average mV
$5x10^{-4}$	52.6	47.9	46.5	45.8	47.2	48.0
$1x10^{-3}$	74.3	73.3	72.3	71.6	71.0	72.5
$5x10^{-3}$	102.9	103.2	103.1	101.6	101.2	102.4
$1x10^{-2}$	114.9	114.6	114.2	113.9	114.2	114.4
$5x10^{-2}$	149.5	148.6	148.0	147.5	146.9	148.1
$1x10^{-1}$	165.3	164.2	165.6	164.2	164.8	164.8
Time, min	1	1.5	2	2.5	3	

The average slope was 51.1 mV/decade, and the correlation was 0.9986 from $5x10^{-3}$ to 10^{-1}M of KCl.

The Na-CWE and K-CWE were retested under the same conditions after a 12 hours period. At this time, both electrodes behaviour indicated a failure to respond to sodium and potassium, respectively.

Three series of determinations were similarly performed with Na-CWE and K-CWE and gave the results depicted in Tables 3.2 and 3.3, respectively. The potential readings of both CWEs described were for stable each series. A constant potential drift was observed during the operational lifetimes of the electrodes. The drift had an average negative magnitude of around 1.7 mV per minute for sodium and positive magnitude of average around 1.1 mV per minute for potassium over 3 minutes period. The slow initial drift, which disappeared following 3 hours of immersion of the electrodes in the solution, can be partly ascribed to the typical asymmetrical arrangement of membrane electrodes with internal solid contacts (metal / membrane / solution). After that, the electrodes showed variations in the potential values of less than a constant average of 1.7 mV/min for Na-CWE, and 1.1 mV/min for K-CWE until the assays were finished.

Another batch of both the Na-CWE and the K-CWE were prepared separately during this investigation and yielded similar results.

3.4.4. Reproducibility of CWEs

The reproducibility of both CWEs were poor. This seemed to be due to such factors as the lack of control over the geometry of the tip, slight cracks suffered during measurements or differences in membrane thickness. In addition, a very low stirring rate had to be used in order to avoid detachment of the membrane from the tip.

3.4.5. Calibration Curves and Response Slopes of CWEs

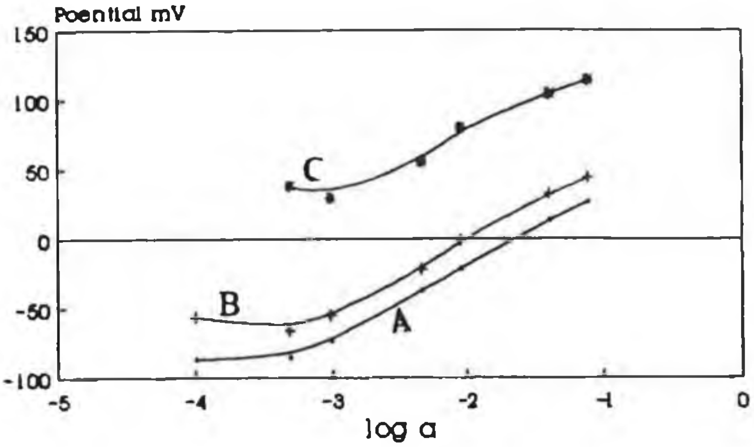


Figure 3.5 Calibration curves for each series of Na-CWE based on ligand N Curve A Series 1, slope = 52.9 mV/decade; curve B Series 2, slope = 52.9 mV/decade; curve C Series 3, slope = 49.2 mV/decade

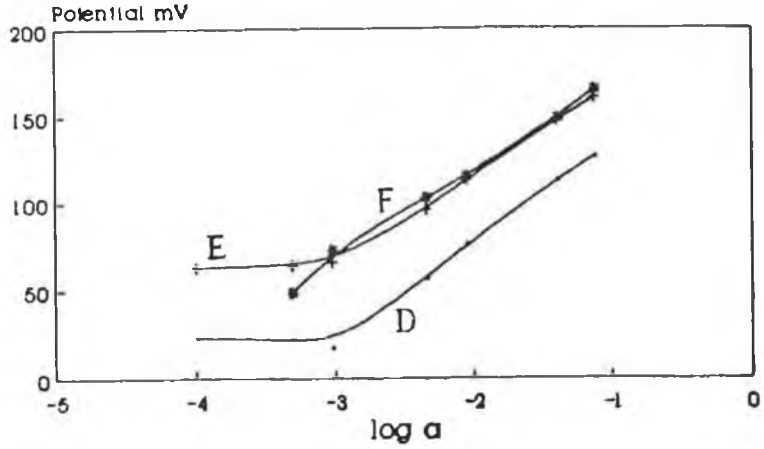


Figure 3.6. Calibration curves for Each Series of K-CWE based on ligand Q Curve D Series 1, slope = 57.6 mV/decade; curve E Series 2, slope = 50.4 mV/decade; curve F Series 3, slope = 51.1 mV/decade

The calibration curve was obtained for each series by using the average potential readings shown in the Tables 3.2. and 3.3 (section 3.4.3). They are shown in the Figures 3.3 and 3.4 above.

The electrode properties of both CWEs were evaluated mainly by the slope and the linear range of the calibration plots. Each CWE fabricated from the same cocktail was calibrated three times over one working day period. Figures 3.5 and 3.6 above illustrate that each series for both electrodes showed a near-Nernstian response in the concentration range from $1x10^{-4}$ to $1x10^{-1}$M for Na-CWE and K-CWE at room temperature. Both electrodes gave a linear potential response over the cation activity from $1x10^{-3}$ to $1x10^{-1}$M. The average slopes were 52.9, 52.9, 49.2 mV/decade for Na-CWE and 57.6, 56.4, 51.1 mV/decade for K-CWE, respectively.

3.4.6. Measurement of Selectivity Coefficients

The selectivity coefficients for these both CWEs were calculated by the classical separate solution method in 0.1 M solutions of alkali metal and alkaline earth ions (see equation 1.5 in section 1.2.1.5). Measurements were taken after 2 minutes immersion in the solution. The results were summarized in Table 3.4.

Table 3.4. Selectivity Coefficients of Both CWEs for sodium and potassium based on ligands N and S respectively.

j=	$K^{Pot}_{Na,j}$	$K^{Pot}_{K,j}$
Na^+	0.0	-0.66
K^+	-0.17	0.0
Li^+	-1.15	-0.77
Rb^+	-0.48	-0.02
Cs^+	-0.47	0.04
H^+	-0.04	1.84
NH_4^+	-0.29	-0.08
Mg^{2+}	-0.44	-0.53
Ca^{2+}	-0.46	-0.36

From Table 3.4 above it can be seen that the order of selectivity for the Na-CWE decreases in the order:

$$Li^+ > Rb^+ > Cs^+ > Ca^{2+} > Mg^{2+} > NH_4^+ > K^+ > H^+ > Na^+$$

Although the Na-CWE shows some ability to discriminate Na ions over the other alkali metals the magnitude of the selectivity coefficients is not very impressive. With regard to the K-CWE, the order of selectivity over interfering ions decreased as follows:

$Li^+ > Na^+ > Mg^{2+} > Ca^{2+} > NH_4^+ > Rb^+ > K^+ > Cs^+ > H^+$

The selectivity data for the K-CWE is also quite poor with positive values of $\log K_{ij}^{pot}$ for Cs^+ and H^+ ions indicating a high response by the electrode to these cationic species. Indeed hexameric calix[6]arenes are well known for their ability to act as caesium selective ionophores so the large response to caesium is not entirely unexpected. Due to the rough and non-uniform nature of the substrate surface, it is feasible that the membrane became thin and porous thus enabling the solution to come in contact with the bare metal. This would result in a substantial loss in selectivity. Following contact of both CWE's with interfering ions during the selectivity coefficient measurements, both electrodes displayed a dramatic loss in response characteristics. Contact of the electrodes with interfering ion solutions may have caused the build up of a poisoning of the active sites due to irreversible complexation of the calixarene with the interfering ions. This will seriously increase the response time and stability of the electrodes.

3.4.7. Dynamic Responses of Both CWEs

The response time of these CWE configurations was also investigated. The dynamic response time of an electrode is a very important factor for practical use of CWEs. The procedure adopted was to add 20 μl of a 1 M solution of alkali metal and alkaline earth ions (Li^+ Na^+, K^+, Cs^+, Rb^+, H^+, NH_4^+, Ca^{2+}, Mg^{2+}) into 20 ml of a 1×10^{-3} M NaCl or KCl solution. The transient responses for CWEs based on ligands N and S are outlined in Figures 3.7 and 3.8 respectively. The final change in potentials are tabulated in Tables 3.5 and 3.6.

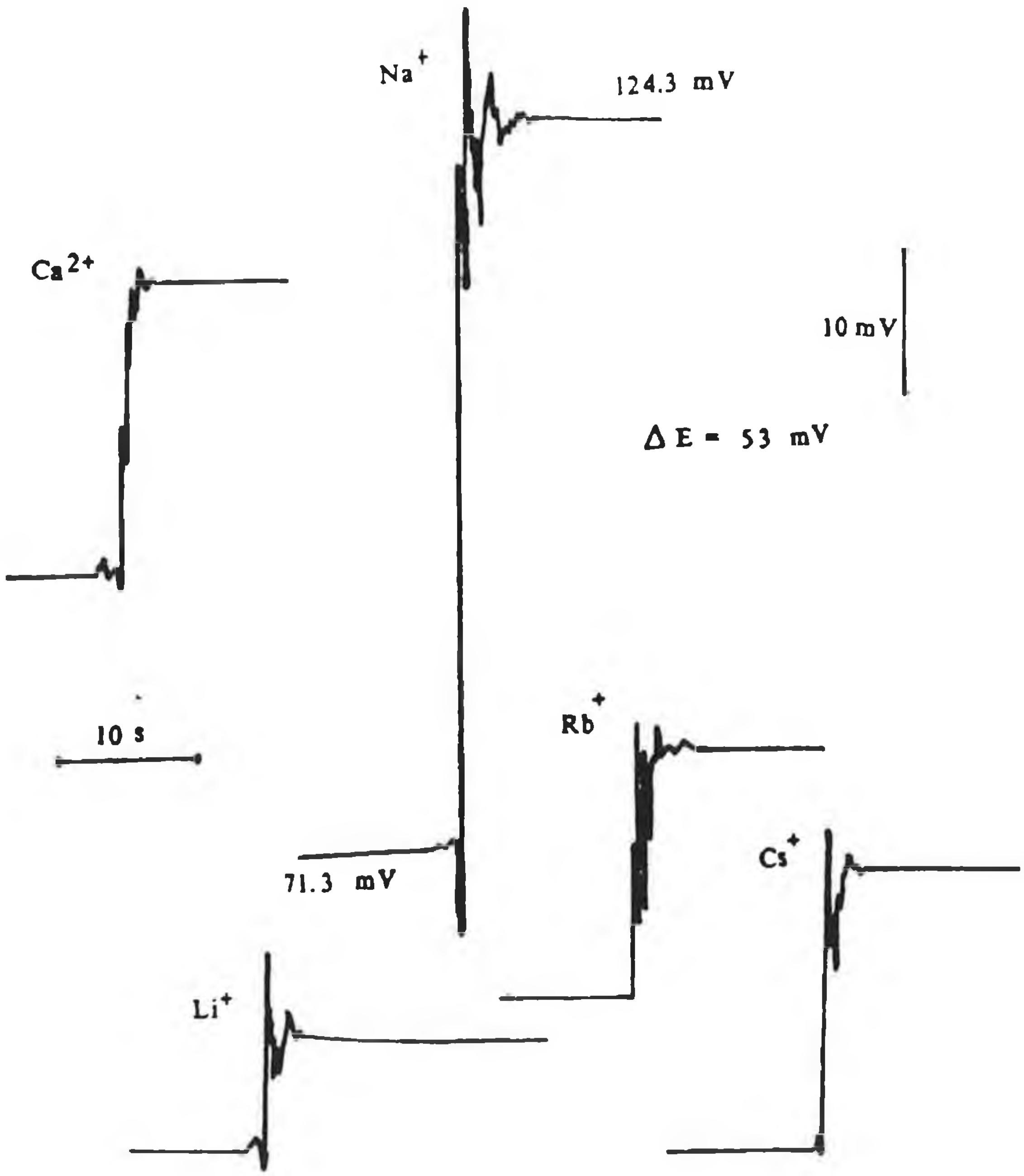
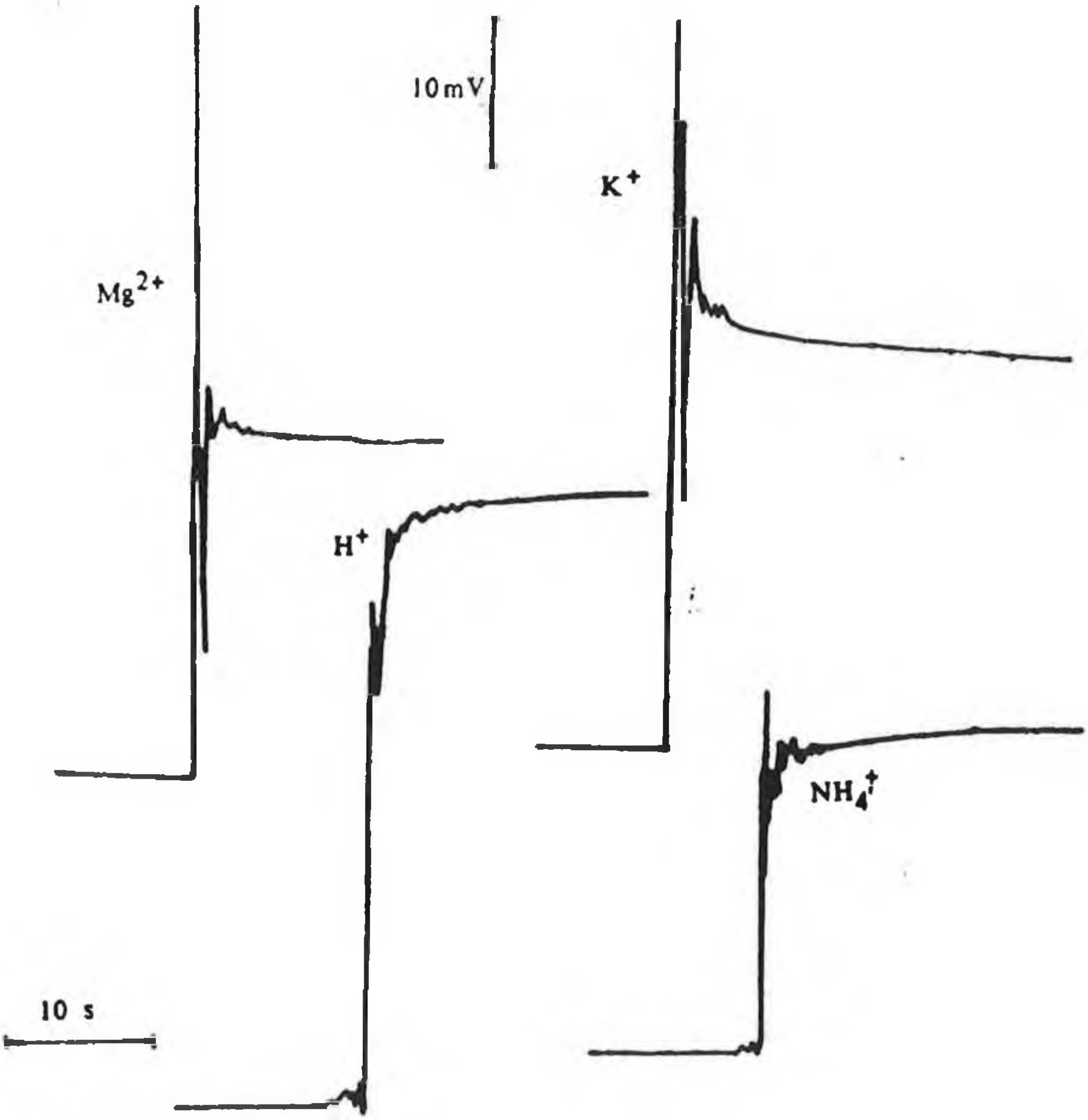


Figure 3.7. Transient response of Na-CWE based on ligand N to injections of 20μl of 1M various metal chlorides into 20 ml of 1x10^{-3}M NaCl solution. Equivalent to an approximate 10-fold increase for a sodium injection (10^{-3} - 10^{-2} M), chart speed 1.0 mm /sec.



(Figure 3.7 continued)

Table 3.5. Response (mV) of Na-CWE following injections of 20μl of 1M alkali and alkaline metal ions into 20 ml of 1x10 ^{3}M NaCl solution

Cation	E_1 mV	E_2 mV	ΔE mV
Na^+	71.3	124.3	53.0
NH_4^+	67.9	92.1	24.2
Li^+	87.4	94.8	7.4
Cs^+	75.4	95.7	20.3
H^+	78.8	121.4	42.6
Ca^{2+}	88.0	108.9	20.9
Rb^+	78.0	96.2	18.2
K^+	88.4	116.4	28.0
Mg^{2+}	82.3	105.9	22.6

E_1 = potential before injection, E_2 = potential after injection and ΔE is the overall change in potential (E_2-E_1).

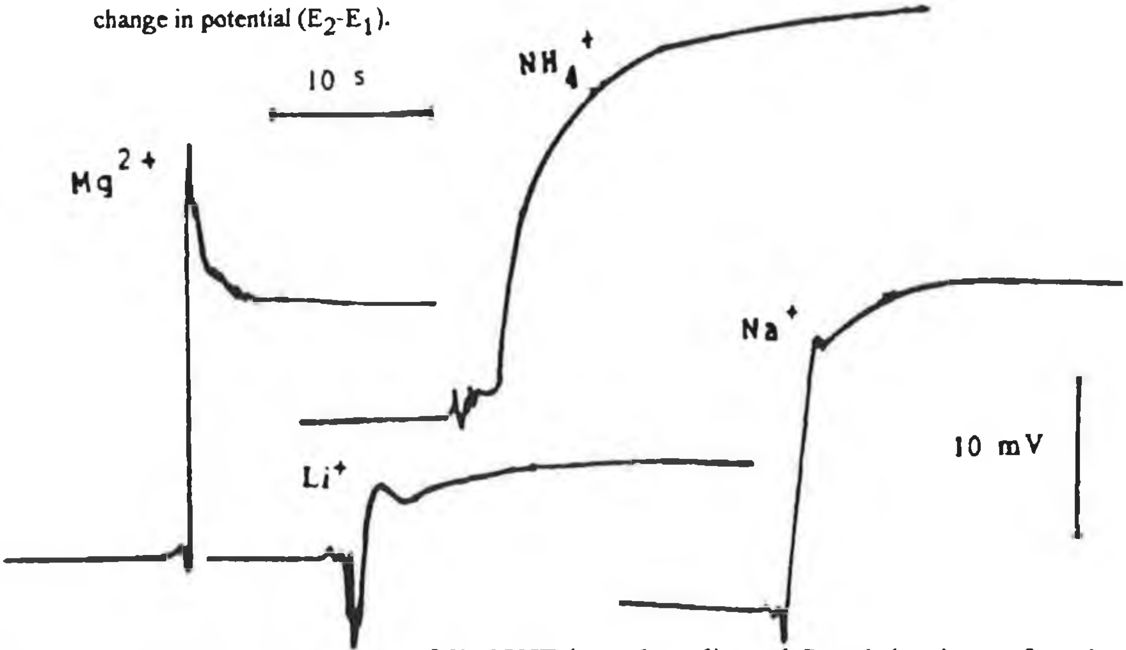
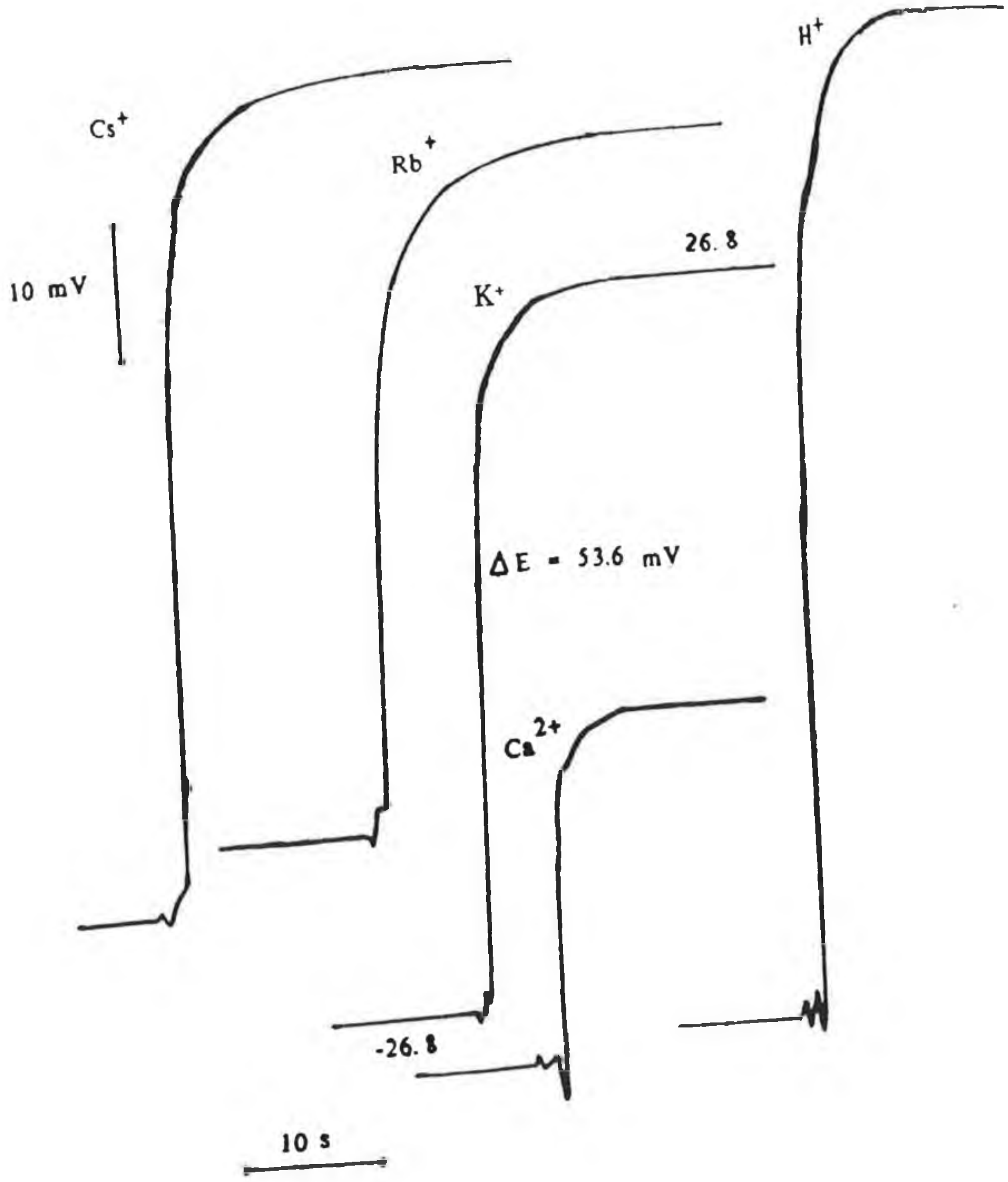


Figure 3.8. Transient response of K-CWE based on ligand S to injections of various cations. Injections as in Figure 3.7, chart speed 1.0 mm /sec



(Figure 3.8 continued)

Table 3.6. Response (mV) of K-CWE following injections of 20μl of 1M alkali and alkaline metal ions into 20 ml of 1x10^{-3}M NaCl solution.

Cation	E_1 mV	E_2 mV	ΔE mV
Na^+	-73.6	-51.5	22.1
K^+	-26.8	26.8	53.6
Li^+	-78.2	-91.5	13.3
Rb^+	-75.1	-23.9	51.2
Cs^+	-79.6	-17.6	62.0
H^+	-75.6	-1.4	74.2
NH_4^+	-76.9	-52.5	26.4
Ca^{2+}	-77.5	-51.6	25.9
Mg^{2+}	--72.1	-56.3	23.8

E_1 = potential before injection; E_2 = potential after injection and ΔE is the overall change in potential (E_2-E_1).

The dynamic responses of both CWEs by the injection of additional solution were very fast for injections of primary and interfering ions < 10 s ($t_{90\%}$) in all cases. The Na-CWE showed a near Nernstian change in potential of 53.0 mV for the sodium response. The next largest change in potential was observed for a HCl injection. The third largest ΔE was obtained by K^+, because Na^+ and K^+ have similar atomic radii. The response to the other alkali and alkaline metal ions were smaller. Hydrogen produced a relatively large response in the Na-CWE. When K^+, Mg^{2+}, Li^+ were injected into the sample solutions, respectively, the magnitude of the response decreased with time and became smaller in comparison to the sodium response only after a couple of seconds. The response of Li^+ was clearly insignificant in comparison with the sodium response. In general the magnitude of the responses reflected the selectivity behaviour shown in the selectivity studies.

For the K-CWE, the result in the case of the K^+ injection showed a Nernstian response (53.6 mV), the response was very fast (see Figure 3.6). The change in potential to injections of HCl, CsCl, RbCl, were rather large. At 73.2 mV for H^+, 52.0 mV for Cs^+, 51.2 mV For Rb^+. This confirms the selectivity coefficient data in Table 3.4 and suggests that the electrode could be used equally well as a caesium or rubidium sensor. Fortunately ions such as caesium and rubidium do not form a natural interfering constituent of many matrices and the high interference from H^+ ions can be controlled by careful use of buffers.

Response time for coated wire electrodes has been found to depend on the amounts of plasticizer in the membrane[38]. The response time increased with a decrease in the amount of plasticizer, and calixarene derivative content in the coated solution also influences the electrode response[38]. The response time, which is a very important factor for practical use of the Na- and K-CWEs based on calix[4]arene and calix[6]arene silylated compounds, was very fast in all cases - within 10 seconds ($t_{90\%}$).

A lot of the unfavourable selectivity characteristics of the electrodes can be attributed to ageing affects of the electrode. After use, particularly with dilute solutions, some of the membrane will dissolve. Unfortunately, it will not dissolve uniformly and the surface will become pitted as illustrated in Figure 3.9 below. Pitting adversely affects both the reproducibility and response time of both electrode. Small volumes of solution will be trapped in the cavities and transferred from one sample to the next.

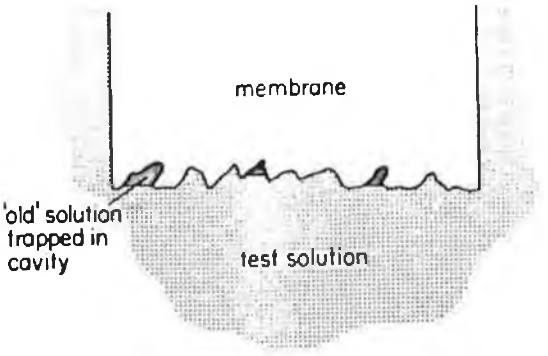


Figure 3.9 Trapping of solution in cavities giving rise to sample carry over when electrode is pitted

3.4.8. Effect of pH on the electrode potentials

The emf of the Na-CWE and K-CWE was influenced by pH of sample solutions. To evaluate further the interference of hydrogen ions on the both CWEs some pH studies were carried out. A pH electrode, reference electrode (SCE) and working electrode (CWE) were inserted into 10 ml of 10^{-3} M NaCl or KCl solution. A few drops of ammonia solution (ca. 1M) was added to adjust the solution to pH 10.5. HCl was then added dropwise to adjust to the pH required. In this way it was possible to monitor simultaneously the solution pH and the potential change at any point in time.

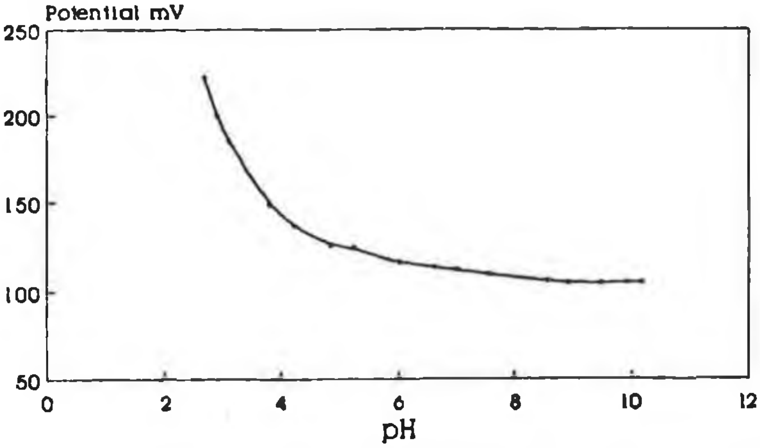


Figure 3.10. The dependence emf of Na-CWE on the pH of solution

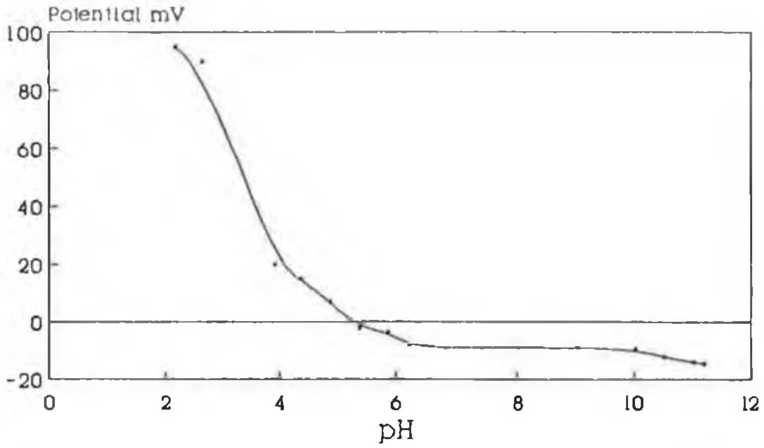


Figure 3.11. The dependence of emf of K-CWE on the pH of solution.

The emf of the Na-CWE and K-CWE were significantly influenced by pH of sample solutions. The effects were even more pronounced in the lower pH region. The emf remained constant in the pH region greater than 7.5 with only insignificant variations in the electrode potentials (less than a few mVs) for Na-CWE with the concentration 10^{-3}M NaCl (as illustrated in Figure 3.10 above). Though the measurements by Na-CWE may be subject to some error at solution pH less than 7.5, the emf of Na-CWE would not be affected by Hydrogen ion concentrations in solutions of basic or neutral pH i.e. the potential response and stability of the electrodes were pH independent over the range pH 6 - 10. Similar results was obtained for K-CWE in Figure 3.11. The pH value remained a constant in the pH region 7 - 10 (negligible potential shifts in the pH more than 7).

3.4.8. Lifetime

The lifetime of CWEs can be an important consideration, the degree of importance depending upon the particular application. The lifetime of both CWEs were short as mentioned above, of the order of 24 hours.

3.5. Conclusion

Both coated wire electrodes incorporating ligand N, and S showed some promise. They exhibited a near-Nernstain response to sodium and potassium, respectively. A definite conclusion of the above experimental CWIs was the fact that, the calixarene membranes gave insufficient protection to the Titanium wire against attack by the chloride ions in the analyte. Although no systematic study was carried out on these electrodes, it has noticed that one important disadvantage of this approach is that the plasticiser and ion-exchanger can leach out of the ionophoric material, into the sample solution thus CWIs the life time and stability of the electrode.

The described coated-wire electrodes have reasonable electrode characteristics and can be produced in a simple way. It is interesting to fabricate such chemical sensors with low costs as disposable devices. In the future it may be possible to manufacture multisensor elements with a reference electrode and a few coated-wire electrodes described above to make for example blood analyses in clinical chemistry more easy. It is also possible to fabricate other electrodes for NH_4^+, H^+, Cl^-, Ca^{2+}, and Mg^{2+} in the same manner as described above. Although the electrodes had a short lifetime of one day, they offer the possibility of mass production of low-cost disposable spot-test sensors for Na^+ and K^+. Although, in terms of over-all performance, these sensors offer no more advantage over other designs they should not be discounted. Their small size and inherent robustness make them ideal for the production of small, solid-state sensors such as ISFETS or hybrid devices. Further work is necessary to improve the adhesive bond between metal and membrane.

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Chapter 4

Chromogenic Calix[4]arene Indicator System Specific for Lithium and Sodium

4.1. Introduction

An area of growing interest in analytical chemistry is the development of optical sensors for the determination of important alkali metal and alkaline earth cations. So far some success has been achieved with chromogenic crown ethers and spherands[1,2]. These new classes of optical sensors are based on conventional, electrically neutral ionophores. These highly selective compounds have been widely applied in membranes of a large variety of ion-selective electrodes[3-10]. By incorporating chromophores near the ion-binding sites, such neutral carriers can dramatically change their absorption spectra in the UV/VIS region on complexation with cations or anions. The advantages of optical sensor devices, in comparison with corresponding electrochemical sensors, are their great versatility, their electrical safety and insensitivity to electrical interference, as well as the fact that no reference device is needed. Calixarenes are strong candidates for chromogenic hosts. Preliminary results describing the synthesis and properties of calixarenes having nitro or azo groups have been reported[11-13]. Shinkai and co-workers have described the design of an ion-selective chromogenic calix[4]arene in which a nitrophenol is used as the chromogenic group in the assembly.

In this chapter, the results from one novel chromogenic ligand based on a calix[4]arene are presented which could form the basis of an optical sensor for lithium and sodium.

4.2. Basic Theory

4.2.1. Theory of Visible and Ultraviolet Spectroscopy

Today the ultraviolet / visible spectrometer is often referred to as the workhorse of analytical laboratory, and is applied to many thousands of determinations which have been developed over the years. Analytical chemists and laboratory technicians regularly use UV / visible spectrometry as an essential tool in the identification and quantification of a very broad range of chemical and biological substances. The equipment for these purposes ranges from very simple colour comparators through to large computer controlled automatic scanning instruments covering the whole of the UV / visible region of the electromagnetic spectrum[14] (see Figure 4.1).

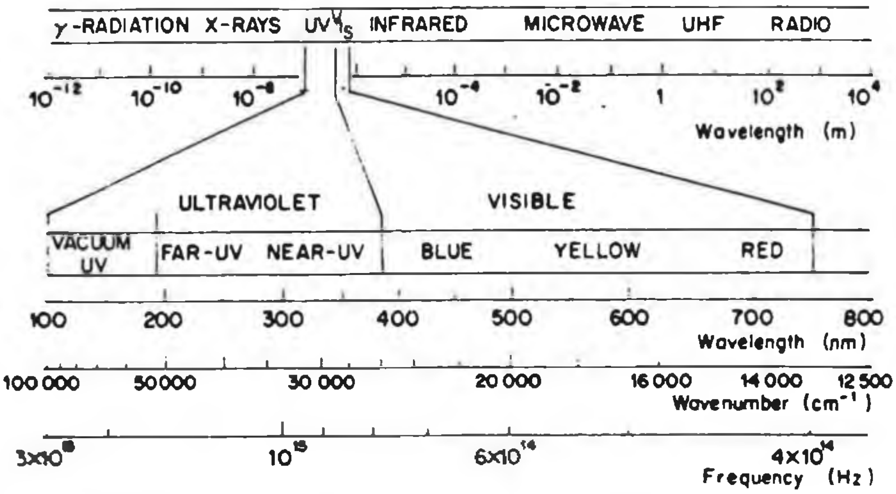


Figure 4.1. The Range of electromagnetic radiation

The general relationship between absorption position, colour of absorbed light in the visible spectrum and resulting colour observed for the transmitted light, is shown in Figure 4.2 (the wavelength range listed define the positions at which the absorption maxima are observed).

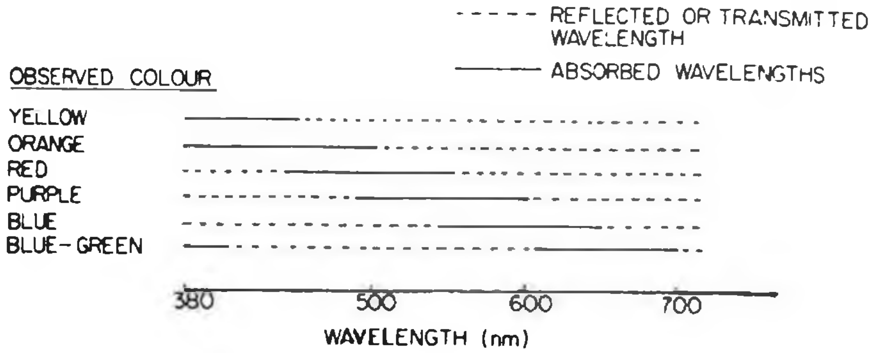


Figure 4.2 Absorption band and colour relationships of the visible spectrum

4.2.2. Complexation Theory

An ionophore which includes an ionisable chromophoric group in its structure (chromoionophore) may respond to cation complexation (see equation 4.1)

$$L\text{-}CH + M^{+} = L\text{-}CM + H^{+} \qquad (4.1)$$

Where:

L = Ligand;

CH = Ionisable chromophore;

M^{+} = Metal ion.

To improve the thermodynamics of this equilibrium, an organic base is normally added or used as a solvent for the ligand / metal ion complexation process (see equation 4.2).

$$L\text{-}CH + B + M^{+} = L\text{-}CM = BH^{+} \qquad (4.2)$$

Where:

B = Base.

A Neutral chromoionophore (CI) contains a polarised chromphore linked to the chromoionophore in such a way that the electrostatic field of a complexed cation changes the absorption spectrum[15].

4.3. Experimental Section

4.3.1. Calixarene Ligand and Morpholine Molecules

The calixarene compounds and morpholine (an organic base) used in this project are showed below.

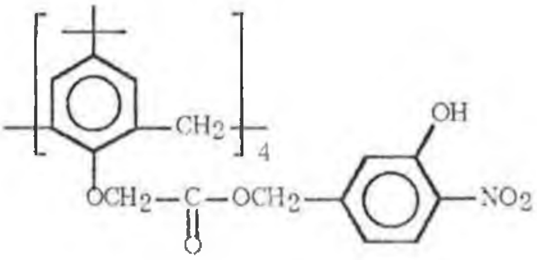


Figure 4.3. Chromogenic nitrocalix[4]arene (ligand R)

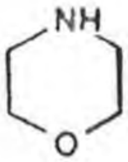


Figure 4.4. The structure of morpholine

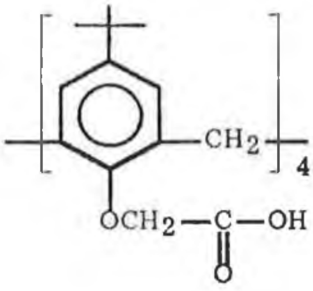


Figure 4.5. The structure of *p - t* -calix[4]arene tetraacetic acid (ligand T)

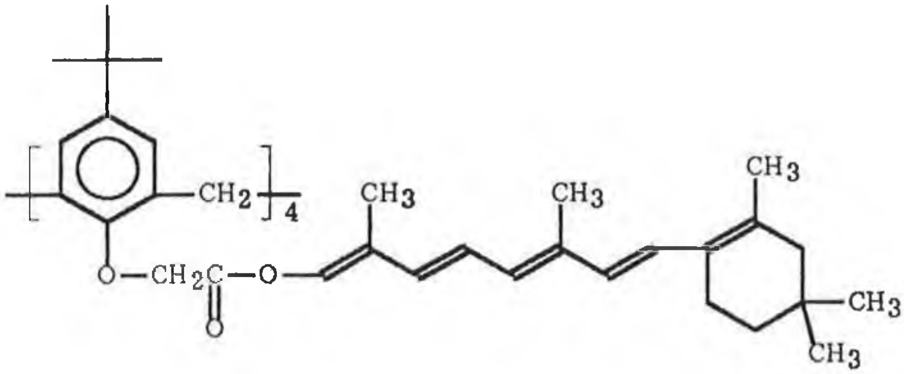


Figure 4.6. The structure of ligand U

4.3.2 Equipment and Reagents

UV/VIS absorbance measurements were taken with a Hewlett Packard 8452A diode array spectrophotometer. pH values of the buffer solutions were determined using a WTW model E 501 glass pH electrode and WTW Model pH 522 pH meter.

Aqueous solutions were prepared in de-ionisied water. The salts LiCl, $LiClO_4$, $NaClO_4$, $KClO_4$, CsCl used were of the highest purity, and were obtained from Reida-de-Haen. Amines: pyridine, n-propylamine n-butylamine, trioctylamine, tertbutylamine, n-methylamine, triethylamine, morpholine were used as bases. Tetrahydrofuran (THF), dichloromethane, acetonitrile, methanol, ethanol and chloroform were used as solvents for the materials.

4.3.3.The Sample Cell

The cell chosen was made of quartz (190 - 820nm) for work in the ultraviolet / visible range. The optical windows were highly polished, flat and parallel and the light path between the inner surfaces of the windows was 10 mm, with a capacity of 4 cm^3 of solution (see Figure 4.7).

Figure 4.7. Quartz cell (open-top normal, with lid)

4.3.4. Nitrocalix[4]arene as Optical Sensor

A chromogenic nitrocalix[4]arene (ligand R) was investigated (chemical structure shown in Figure 4.3 in section 4.3.1). This chromoionophore contains a 4-nitro-3-phenol unit as the chromophore.

4.3.5. General Procedures

Ligand R was dissolved in freshly dried THF, to give a $5x10^{-5}M$ solution. A 5ml volume of the sample solution was transferred by pipette into a stoppered test-tube and $2.3x10^{-5}M$ morpholine was added, followed by known amounts of LiCl or $LiClO_4$ or $NaClO_4$ solution, respectively. A dramatic colour change from colourless to yellow took place rapidly. Before spectroscopic analysis, the tube containing the mixture was shaken in a ultra sonic bath for 5 minutes and allowed to stand for at least one hour.

As the instrument is a single-beam, diode array system, a blank is initially scanned and stored on disc. This is subtracted from the subquent sample scans. Valid data were obtained over the spectral range 210 - 820 nm and the data saved on disc.

4.4. Results and Discussion

4.4.1. Using of the Sample Cell

Before the cell is used, it needs to be cleaned with de-ionisied water and ethanol at least three times, alternatively. The cell should then be rinsed several times with the sample solution and filled with sample to within 1 cm of the top. The outer surfaces should be perfectly clean, dry and show no signs of finger marks or smears. Avoid wiping the optical surface by transferring the washes and sample in a way that avoids spilling down the outside of the cell e.g. by using disposable pipettes.

4.4.2. Experimental Design

From the optical point of view the solvent should be transparent in the region of measurement, and should be of consistent purity and its important characteristics include adequate solubility of the ligand and salts, and stable interactions with the absorbing species. The solubility of ligand R in the solvents investigated in this study are listed in Table 4.1.

Table 4.1 Solubility of ligand R and salts in solvents

Solubility	CH_3CN	THF	CH_3OH	CH_2Cl_2	$CHCl_3$	C_2H_5OH
Ligand R	NO	YES	YES	YES	YES	YES
Li^+ (or Na^+)	NO	YES	YES	NO	NO	YES

These results show that CH_3CN, $CHCl_3$, CH_2Cl_2 could not be used due to insufficient solubility of the salts in these solvents. On the other hand, CH_3OH, C_2H_5OH and THF were able to dissolve the salts LiCl, NaCl, $LiClO_4$, $NaClO_4$ and ligand R. CH_3OH was examined initially but found to react with the Li^+ / Na^+ ions, inhibiting the ion-ligand reaction and hence the generation of the coloured complex (see equation 4.3).

$$Na^+(\text{ or } Li^+) + CH_3OH = CH_3ONa (\text{ or } Li^+) + H^+ \qquad (4.3)$$

A similar phenomenon occurred with C_2H_5OH and this was also abandoned for further work. Tetrahydrofuran (THF) proved to be an ideal solvent. It can dissolve the ligand R, $LiClO_4$, $NaClO_4$, and trace LiCl, NaCl and so it was chosen as the solvent for subsequent investigations.

In early work, a two phase system (organic and aqueous phases) were tried (CH_2Cl_2 was used as organic solvent). Ligand R can be dissolved in CH_2Cl_2, and metal ions can be dissolved in water. Tris buffer was used to control and adjust the system's pH value. However, it was observed that the colour generated by the ion-ligand complexation moved into the aqueous layer.

These results suggest that on complexation, the coloured complex partition into the aqueous layer in preference to the organic. While this is not desirable from a sensor point of view (as the sensor molecule should not leach from the sensor into the aqueous sample). It raises interesting question as to what is happening to the molecule to render in the complex water soluble.

4.4.3. Morpholine Effects

The chemical structure of morpholine is shown in Figure 4.4 in section 4.3.1. The effects of morpholine on the chromoionophoric reaction have been studied. The experimental method was as follows: The ligand R was dissolved in THF and diluted to $5x10^{-5}$ M. Six 5 ml samples containing a fixed amount (0.004 M) of $NaClO_4$ and ranging morpholine content were prepared. The morpholine content was 0, $2.3x10^{-5}$

M, 4.6x10^{-5}M, 6.9x10^{-5}M and 9.2x10^{-5}M. The compositions are summarised in Table 4.2 below. The blank contained 5x10^{-5}M ligand R and 0.004M $NaClO_4$ in THF.

Table 4.2 Investigation of the effect of morpholine: the Composition of the Solutions

Sample	Ligand R, M	$NaClO_4$, M	Morpholine, M
A	5x10^{-5}	4x10^{-3}	0
B	5x10^{-5}	4x10^{-3}	2.3x10^{-5}
C	5x10^{-5}	4x10^{-3}	4.6x10^{-5}
D	5x10^{-5}	4x10^{-3}	6.9x10^{-5}
E	5x10^{-5}	4x10^{-3}	9.2x10^{-5}

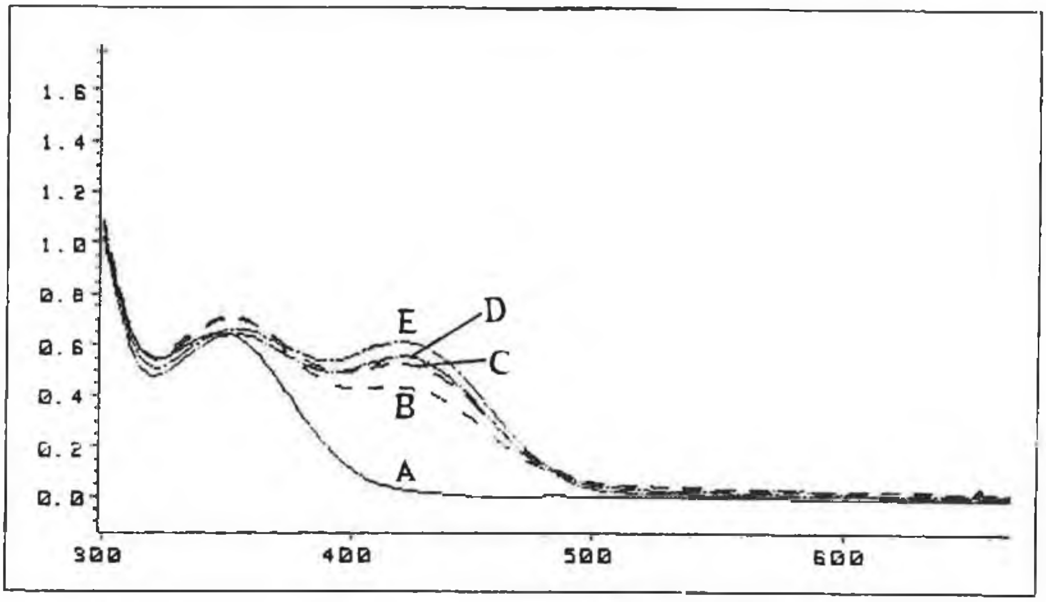


Figure 4.8 Effect of morpholine effecting on UV / VIS absorbance of ligand R in the presence of Na^+ system

curve A no morpholine; curve B 2.3x10^{-5}M morpholine; curve C 4.6x10^{-5} M morpholine; curve D 6.9x10^{-5}M morpholine; curve E 9.2x10^{-5}M morpholine

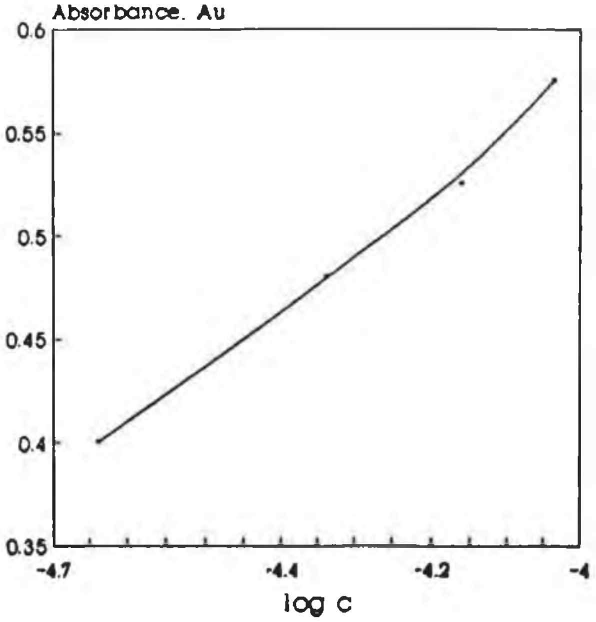


Figure 4.9 log concentrations versus absorbances (morpholine the wavelength is in the 420 nm)

In early work, many bases were tried including pyridine, *n* - propyl-amine, *n* - butylamine, trioctylamine *t*- butylamine *n*-methylaniline, and triethylamine, but no colouration occurred even in the presence of alkali metal cations. Colouration occurred only in the presence of the amine morpholine. These results demonstrate that morpholine is a strong enough base to enable the proton to leave the chromoionophore on complexation with the metal ion.

With respect to Figure 4.8, curve A was obtained before any morpholine was added from the lack of absorbance around 420nm, it seems that the ligand R was unionised.

Curves B, C, D and E were obtained by additions of 2.3×10^{-5}M, 4.6×10^{-5}M, 6.9×10^{-5} M, 9.2×10^{-5}M morpholine, respectively. The spectra changed with increasing concentrations of morpholine, with a large increase in absorbance around 420 nm. The importance of morpholine was confirmed by the total lack of spectral changes on addition of metal salts in the absence of morpholine. This phenomenon indicates why the other amines were not suitable.

Figure 4.9 shows that under the conditions of this particular study, a limit value of around 4.6×10^{-5}M morpholine was needed to ensure efficient generation of the coloured complex in the presence of sodium ions. This amount was chosen for use in further studies.

4.4.4. Nitrocalix[4]arene as a Lithium and Sodium Colorimetric Indicator

Anhydrous lithium perchlorate and sodium perchlorate were used. Different amounts of crystalline $LiClO_4$ and $NaClO_4$ were added directly to the sample solutions. The blank and sample solution compositions are outlined in Tables 4.3 and 4.4 below.

Table4.3. The composition of the solutions for lithium experiments

Sample, No.	Ligand, M	Morpholine, M	$LiClO_4$, M
A	5×10^{-5}	4.6×10^{-5}	2×10^{-5}
B	5×10^{-5}	4.6×10^{-5}	8×10^{-4}
C	5×10^{-5}	4.6×10^{-5}	4×10^{-3}
D	5×10^{-5}	4.6×10^{-5}	1×10^{-2}
E	5×10^{-5}	4.6×10^{-5}	1×10^{-1}

Blanks as for samples but without ligand.

Table 4.4. The composition of the solutions for Sodium experiments

Sample, No.	Ligand, M	Morpholine, M	$NaClO_4$, M
A	$5x10^{-5}$	$4.6x10^{-5}$	0
B	$5x10^{-5}$	$4.6x10^{-5}$	$8x10^{-4}$
C	$5x10^{-5}$	$4.6x10^{-5}$	$4x10^{-3}$
D	$5x10^{-5}$	$4.6x10^{-5}$	$2x10^{-2}$
E	$5x10^{-5}$	$4.6x10^{-5}$	$1x10^{-1}$
F	$5x10^{-5}$	$4.6x10^{-5}$	$1.4x10^{-1}$
G	$5x10^{-5}$	$4.6x10^{-5}$	$4x10^{-1}$

Blanks as for samples but without ligand.

On addition of the metal ion to the samples, the colour changed rapidly from colourless to yellow, with the colour density being dependent on the amount of metal. The spectra were obtained from the UV / VIS system by scanning the blank and sample solutions, respectively. For example, 4ml blank solution consisting of $2x10^{-5}$M $LiClO_4$ in THF with $4.6x10^{-5}$M morpholine was transferred into the cell by pipette. The scanning started after the cell was put in the cell holder, and then 4ml sample solution which consisted of $2x10^{-5}$M $LiClO_4$ and $5x10^{-5}$M ligand R in THF with $4.6x10^{-5}$M morpholine was scanned. The spectra were obtained according to this procedure. Similar experiments were carried out in which $LiClO_4$ was substituted with $NaClO_4$. The spectra of all the samples were overlaid (see Figures 4.10 and 4.12).

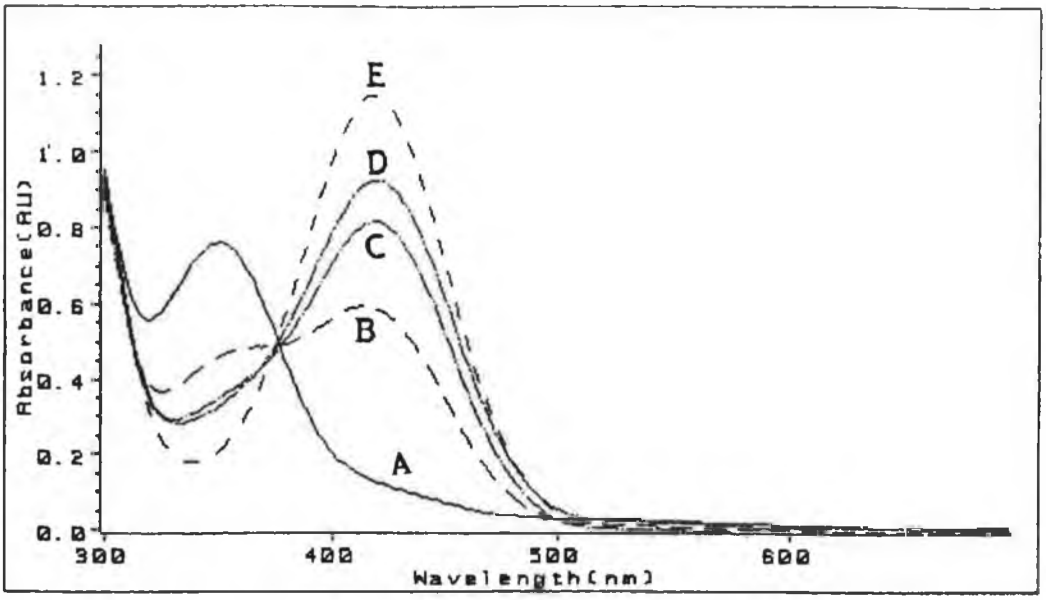


Figure 4.10 Changes in electronic spectra of $5x10^{-5}$M ligand R in 5ml THF with $4.6x10^{-5}$M morpholine containing different concentrations of $LiClO_4$ curve A, $2x10^{-5}$M $LiClO_4$; curve B $8x10^{-4}$M $LiClO_4$; curve C $4x10^{-3}$M $LiClO_4$; curve D $1x10^{-2}$M $LiClO_4$; curve E $1x10^{-1}$M $LiClO_4$

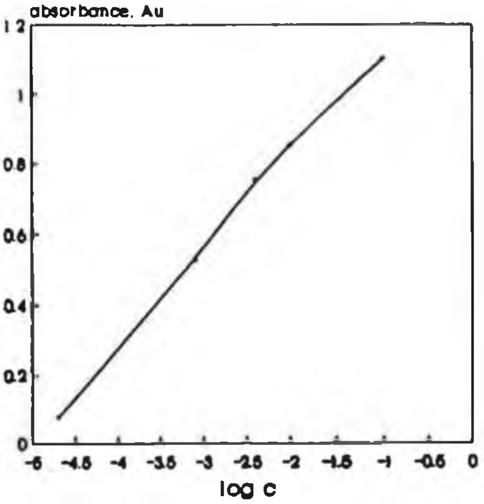


Figure 4.11 The calibration curve of the lithium experiments

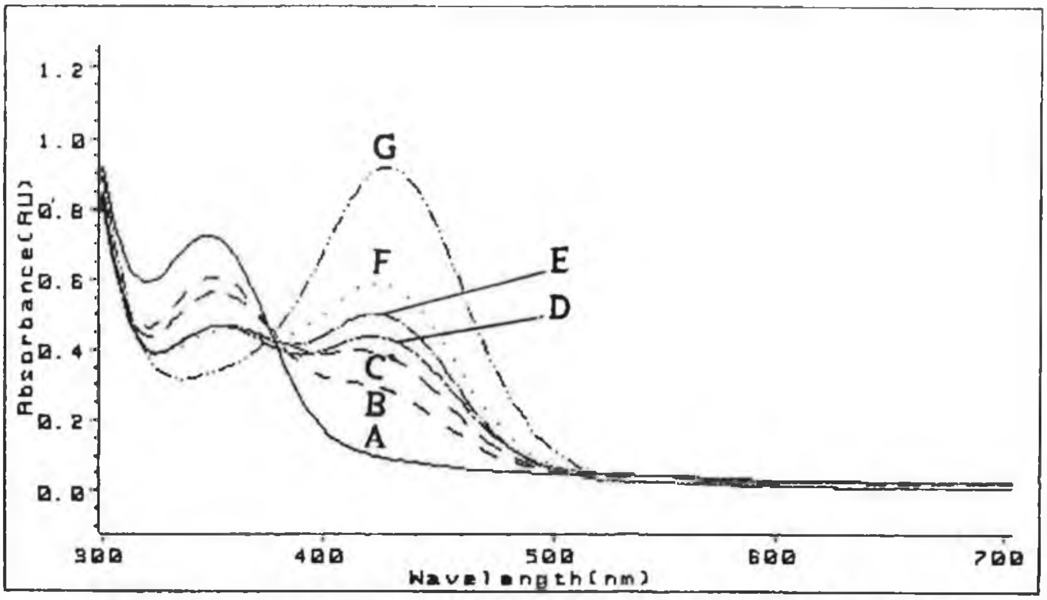


Figure 4.12 Changes in electronic spectra of $5x10^{-5}M$ ligand R in 5ml THF with $4.6x10^{-5}M$ morpholine containing different concentrations of $NaClO_4$ curve A no $NaClO_4$; curve B $8x10^{-4}M$ $NaClO_4$; curve C $4x10^{-3}M$ $NaClO_4$; curve D $2x10^{-2}M$ $NaClO_4$; curve E $1x10^{-1}M$ NaClO4; curve F $1.4x10^{-1}M$ $NaClO_4$; curve G $4x10^{-1}M$ $NaClO_4$

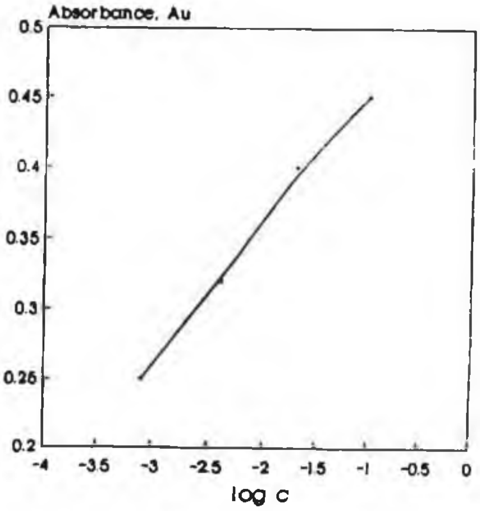


Figure 4.13 The calibration curve of the sodium experiments

Figure 4.10 shows the changes in the absorbance spectra of ligand R in THF with $4.6x10^{-5}M$ morpholine caused by varying concentrations of $LiClO_4$. Note that there was no difference between curve A ($2x10^{-5}M$ $LiClO_4$) and a scan of a sample containing no $LiClO_4$. However, with the addition of more than $2x10^{-5}M$ $LiClO_4$, complexation occurred instantaneously. Lithium ion specific complexing occurred in a base solution of calix[4]arene having one nitrophenol unit. It was clear that addition of lithium ion caused a large change in the absorbance spectra. As is evident, in the overlaid spectra (Figure 4.10), the maximum change in absorbance with various sample concentrations is at a wavelength of 420nm with an isosbestic point at 370nm in the case of ligand R. Similar results were obtained with $NaClO_4$ (see Figure 4.12). The colouration took place only when the specimen was in contact with Li^+ or Na^+. In THF, no deprotonation of ligand R was detected in the absence of metal ions even in the presence of morpholine (see Figure 4.8 curve A). When crystalline lithium or sodium perchlorate was added to this solution, a colour change occurred immediately. So the complexation was occurring between ligand R and Li^+ or Na^+, and the complexation ability was metal ion concentration dependent.

4.4.5. Comparison of the Spectra for Lithium, Sodium, Potassium and caesium

The spectra were obtained with blanks containing $4x10^{-3}$ M $KClO_4$ (or CsCl), $4.6x10^{-5}M$ morpholine, in THF and sample of $4x10^{-4}$ M $KClO_4$ (or CsCl), $4.6x10^{-5}M$ morpholine $5x10^{-5}$ M ligand R in THF. Figure 4.14 was obtained by overlaying these spectra with curve C in Figure 4.10, and curve C in Figure 4.12.

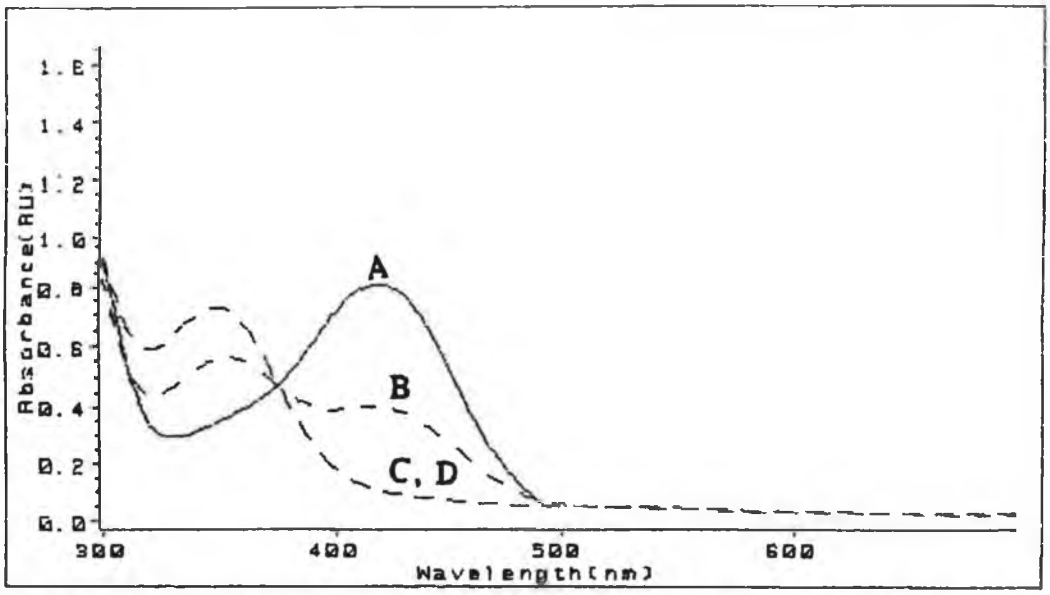
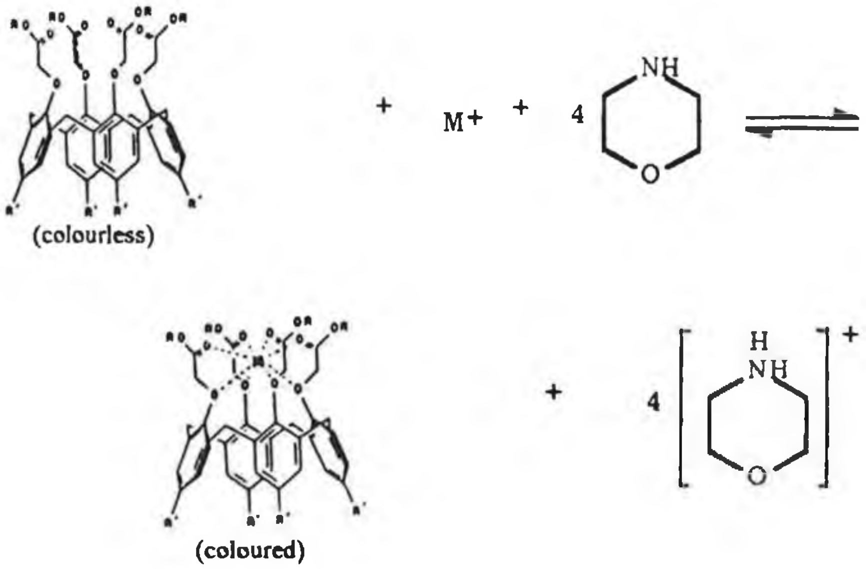


Figure 4.11 Comparision of the spectra for lithium perchlorate, sodium perchlorate, potassium perchlorate and caesium chloride

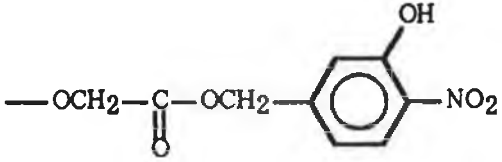
curve A $4x10^{-3}$ M $LiClO_4$; curve B $4x10^{-3}$M $NaClO_4$; curve C $4x10^{-3}$ M $KClO_4$; curve D $4x10^{-3}$ M CsCl

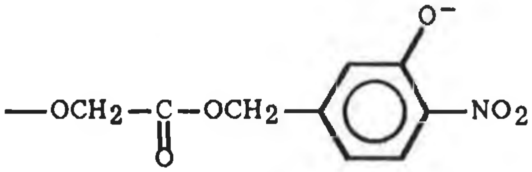
It was apparent that the selectivity of this chromogenic calix[4]arene colorimetric indicator was in the order Li > Na > K, Cs. The substitution of ultrapure $KClO_4$ or CsCl for the $LiClO_4$ or $NaClO_4$ resulted in no colour change. This is probably because potassium or caesium ions are too large to enter the ionophore cavity (radius is 0.3 to 0.33 nm)[16] (see Figure 4.3 in the section 4.3.1). Apparently this ligand R is a strong enough complexing agent to break up the lattice of crystalline $LiClO_4$ or $NaClO_4$ (see equation 4.4). Thus reaction occurred with Li^+ or Na^+, but not with Cs^+ or K^+ (Li atom radius is 0.152 nm; Na atom radius is 0.186 nm; K atom radius is 0.227 nm; and Cs atom radius is 0.265 nm)[17].



where:

R' = *t*- butyl;

R =


R'' =


4.4.6. Chromogenic Nitrocalix[4]arene

With the intention of achieving much higher selectivity for Lithium or sodium ion complexation, the *p* - *t* -Calix[4]arene tetraacetic acid (ligand T) in Figure 4.5 section 4.3.1 was modified by attachment of a nitrophenol moiety to form the nitrocalix[4]arene. This host gave shifts in the wavelength upon complexation of the alkali metal ions Li^+ and Na^+. In the hydrophobic solvent THF, lithium and sodium ions can be accommodated in the hydrophilic cavity of the host as predicted from the cavity dimension of such molecules.

So the observed preferred lithium or sodium selectivity under the given experimental conditions can be explained in terms of binding the guest ions by coulombic attraction and ion-dipole interactions, and rejecting larger or multi cations by the steric effect caused by the narrow entrance to the small cavity of ligand R.

In early work, ligand U was studied (see Figure 4.6 in section 4.3.1). According to the same method as with ligand R. No coloration appeared.

4.4.7. Injection Experiment

1M LiCl solution was diluted to 10^{-1}M and 10^{-2}M by deionised water. 10μl of 1M, 10^{-1}M, 10^{-2}M LiCl were injected to 5ml THF with 4.6×10^{-5} M morpholine by a micropipette to give the following concentration of LiCl, respectively (see Table 4.5).

Table 4.5. The composition of the solutions for injection experiment

Sample, No.	Ligand, M	Morpholine, M	LiCl, M
1	5x10^{-5}	4.6x10^{-5}	2x10^{-5}
2	5x10^{-5}	4.6x10^{-5}	2x10^{-4}
3	5x10^{-5}	4.6x10^{-5}	2x10^{-3}

Blanks as for samples but without ligand.

These three spectra obtained were overlaid (see Figure 4.15), with the spectra containing $LiClO_4$ in order to compare the effects of various anions.

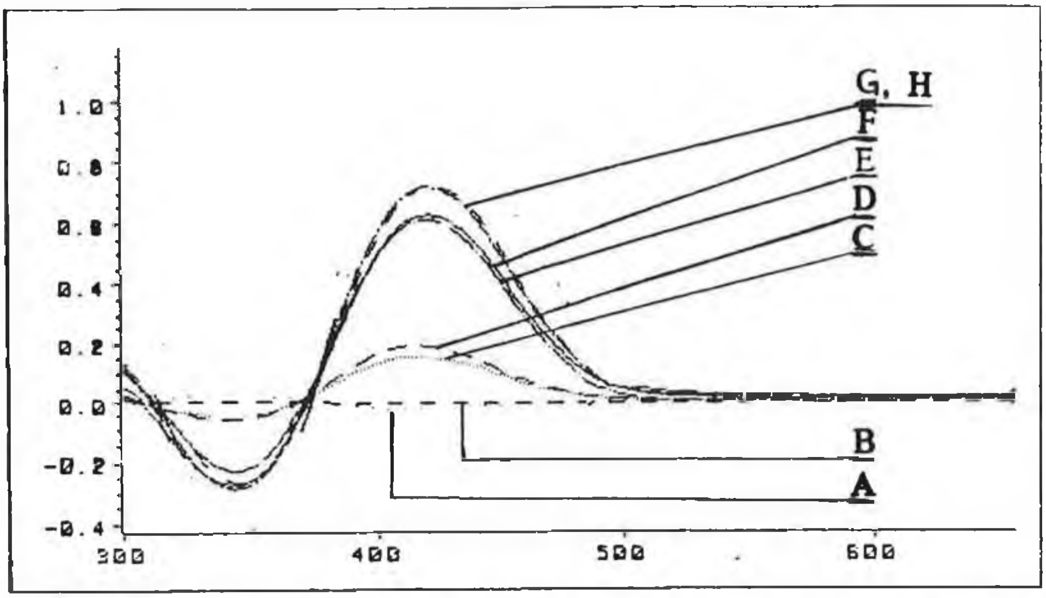


Figure 4.15. Comparison anions effect (ClO_4^- and Cl^-) on Li^+ complexation with ligand R

curve A $2x10^{-5}$ M LiCl; curve B $2x10^{-5}$ M $LiClO_4$; curve C $8x10^{-5}$M LiCl; curve D $8x10^{-5}$M $LiClO_4$; curve E $4x10^{-4}$M LiCl; curve F $4x10^{-4}$M $LiClO_4$; curve G $1x10^{-3}$M LiCl; curve H $1x10^{-3}$ M $LiClO_4$

With regard to the lithium salts, only lithium perchlorate can be directly dissolved in the hydrophobic solvent THF. For the other lithium salts, their chloride salts of lower concentration can be dissolved in THF by injecting. Because THF has poor solubility to water, only trace amounts can be dissolved. Hence the concentration range from $2x10^{-5}$M to $1x10^{-3}$M of LiCl was chosen for study. Above this range, the sample becomes cloudy due to excess water resulting in significant scattering of UV radiation; below this range, the concentration was difficult to obtain. The results of LiCl were almost the same as that of $LiClO_4$ (see Figure 4.15). Similar experiments with sodium chloride produced the same spectral response.

4.5. Conclusion

The chromogenic nitrocalix[4]arene can be as a lithium or sodium-specific chromogenic indicator system for lithium or sodium ions in the presence of morpholine as a base. It is clear that addition of lithium or sodium ions causes a large change in the absorbance 420 nm and isobestic point at 370 nm. The crucial role played by the base in generating the optical response was confirmed by the total lack of spectral changes on addition of metal salts in the absence of morpholine. These results have demonstrated that the chromogenic nitrocalix[4]arene will have important applications in the future in the development of optical sensors and colorimetric reagents for the determination of lithium or sodium ions. Particularly in blood, the lack of response to potassium ions suggests that ligand R may be useful for sodium determinations in the absence of lithium.

4.6. References

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