



e-ISSN: 2319-8753 | p-ISSN: 2347-6710

# IJRSET

International Journal of Innovative Research in  
**SCIENCE | ENGINEERING | TECHNOLOGY**

# INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH

IN SCIENCE | ENGINEERING | TECHNOLOGY

Volume 10, Issue 10, October 2021

**ISSN** INTERNATIONAL  
STANDARD  
SERIAL  
NUMBER  
INDIA

Impact Factor: 7.569

9940 572 462

6381 907 438

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[www.ijrset.com](http://www.ijrset.com)

# Extraction and Transport Studies of Cations Using Azo Group Containing Ionophores Through Liquid Membrane

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**ABSTRACT:** A new series of noncyclic chromogenic ionophores, i.e. 1-(1-(4-(phenyldiazenyl)phenyldiazenyl)-2-naphthalenyloxy)anthracene-9,10-dione (M<sub>1</sub>), 1-(1-(4-(phenyldiazenyl)-2-naphthalenyloxy)anthracene-9,10-dione (M<sub>2</sub>), 1-(4-(phenylazo)phenylazo)-2-naphthol (M<sub>3</sub>) and 1-(phenylazo)-2-naphthol (M<sub>4</sub>) were used in liquid-liquid extraction and liquid membrane transport studies of alkali metal ions. Ionophores M<sub>1</sub> and M<sub>2</sub> have been synthesized and characterized by m.p., T. L.C. and spectral analysis and M<sub>3</sub>, M<sub>4</sub> were commercially available. The effect of various parameters, such as variation in concentration of metal ion as well as ionophore and the effect of anions, have been studied. The sequence of metal ions extracted by M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub> and M<sub>4</sub> ionophores were K<sup>+</sup> > Na<sup>+</sup> and transported by M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub> and M<sub>4</sub> ionophores were Na<sup>+</sup> > K<sup>+</sup>. The effect of anions on the extraction and transport for M<sub>1</sub>, M<sub>2</sub> ionophores was Pic<sup>-</sup> > Dnp<sup>-</sup> > Onp<sup>-</sup>; the observed trend for M<sub>3</sub>, M<sub>4</sub> ionophores was Dnp<sup>-</sup> > Pic<sup>-</sup> > Onp<sup>-</sup> for extraction and Pic<sup>-</sup> > Dnp<sup>-</sup> > Onp<sup>-</sup> for transport. Ionophores deserve special attention because of their applications in separation technology, ion selective electrodes help in understanding the model of ion transport across liquid membrane.

**KEYWORDS-** Azo, extraction, transport, ionophores, liquid, membrane

## I. INTRODUCTION

The extraction and carrier facilitated transport of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> picrates dinitrophenolates, orthonitrophenolates and thiocyanates were studied using triethylene glycol monomethyl ether as a carrier through chloroform, 1,2 dichloroethane and carbontetrachloride bulk liquid membranes. K<sup>+</sup> and Ca<sup>2+</sup> were selectively extracted into the organic phase over Na<sup>+</sup> and Mg<sup>2+</sup>. The ionophore is an efficient carrier for transport of Na<sup>+</sup> and Ca<sup>2+</sup> over K<sup>+</sup> and Mg<sup>2+</sup>. Higher extraction of cations was observed in CH<sub>2</sub>ClCH<sub>2</sub>Cl than in CHCl<sub>3</sub> and CCl<sub>4</sub>, while the amount of cations transported was the same in all the solvents. The anion has no effect on extraction and transport of cations. This ionophore is an efficient extractant and carrier for transport of both alkali and alkaline earth metal ions. Azobenzene derivatives due to their photo- and electroactive properties are an important group of compounds finding applications in diverse fields. Due to the possibility of controlling the trans-cis isomerization, azo-bearing structures are ideal building blocks for development of e.g. nanomaterials, smart polymers, molecular containers, photoswitches, and sensors. Important role play also macrocyclic compounds well known for their interesting binding properties. In this article selected macrocyclic compounds bearing azo group(s) are comprehensively described. Here, the relationship between compounds' structure and their properties (as e.g. ability to guest complexation, supramolecular structure formation, switching and motion) is reviewed. Extraction of metal cation through liquid membrane is one of the important application of supramolecular chemistry. This work investigates the use of synthetic carrier (ionophore) for the extraction of transition metal cations. In this work effect of light on extraction of metal cations through chromophoric ionophore have been tested. For this purpose, a non-cyclic ionophore, 1-phenylazonaphth-2-ol has been used to extract transition metal cations (Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup>). Chloroform is used as a solvent. The extracted amount of metal cations depends mainly upon the structure and the concentration of the ionophore and also on the concentration of metal ions. These studies were focused on the capacity of the ionophore to extract metal cation from an aqueous phase into an organic phase by complexation. On comparing the results of extraction of metal cations (Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup>) with ionophores 1-phenylazonaphth-2-ol in the presence of artificial light source (100W) and natural light it is observed that these ionophores exhibit the photo responsive properties. [1,2,3]

## II. DISCUSSION

Supramolecular chemistry can be defined as a field of chemistry, which studies the complex multi-molecular species formed from molecular components that have relatively simpler structures. This field has been subject to extensive research over the past four decades. Scientists involved in supramolecular science design and study new

chemical systems that are bound together reversibly by intermolecular forces, rather than by conventional covalent bonds (shared electrons). The field exploded when three of the pioneers of the field namely, Jean-Marie Lehn, Donald Cram and Charles Pedersen won the 1987 Nobel Prize in chemistry for synthesizing molecules and compounds with cavities and cages within which metal ions and other molecules could be bound. Research teams have also presented their pioneering works on the syntheses in the field. The syntheses majorly focus on specific groups of compounds, which, although a bit frightening for those out of the field, are invaluable to the experienced researcher. [4,5,6]

One can also find examples of other synthetic methods in a number of undergraduate practical guides; however, these are not usually counted as being related to the supramolecular context. Other routine methods for the synthesis of supramolecules are available in the organic syntheses literature.

What is “Supramolecular” Chemistry? The origin of supra molecular chemistry is closely linked to Pederson's pioneering works on crown ethers. He discovered dibenzo [18] crown-6 in 1967, while he was trying to prepare a flexible phenol terminated polyether. He wanted the polyether to use it to support the catalytic activity of vanadyl ion, by binding to it [1]. Although the importance of this new class of compounds was globally recognized, scientists were still interested in the potential of polyethers to act as metal binding ligands. Most of the scientists started synthesizing new compounds using polyethylene glycols and tried to modify them. Further experiments by Vögel and Weber led them to suggest the term podants for the family of compounds they synthesized [2].

Since a very long time ago, the term “Supramolecular” has been used to refer to complicated bio-structures. The application of this terminology for referring to molecular interactions has its roots in Lehn's Nobel Prize (1987). He described this word as “chemistry beyond the molecule” [3].

Scientists have analyzed natural systems and extracted two major principles involved in supramolecular chemistry molecular recognition and self-assembly.

In molecular recognition, a molecule “host” will combine with a molecule “guest”. In self-assembly, molecular structures of a defined geometry add complementary molecular components, becoming ever-larger arrays. Chemists, biologists, engineers, physicists, optical scientists and materials scientists are effectively “architects” who apply the fundamental principles involved in the biological processes to design and fabricate artificial supramolecular systems. Because of this approach, supramolecular chemistry will have a major impact on materials science in the next century.

Supramolecular chemistry has been referred to, using other names including “host-guest chemistry”, “molecular recognition”, and “inclusion phenomena” [4].

Although the mentioned terms maybe a useful key words for searching in the literature they are not the answer one may require to the question of what exactly makes a particular aspect of chemistry “supramolecular”.

Here, due to the focus of this article on specific applications of supramolecular chemistry, in the construction of potentiometric sensors, host-guest aspect of supramolecular chemistry is taken into consideration. [7,8,9]

Host-guest chemistry, as mentioned above, describes complexes that are composed of two or more molecules or ions that are held together in unique structural relationships by either or a combination of hydrogen bonding or by ion pairing or by Van der Waals force, or forces other than those of full covalent bonds.

The host component is defined as an organic molecule or ion, whose binding sites converge in the complex and the guest component, is defined as any molecule or ion whose binding sites diverge in the complex. To make it more clear let us give an example. In an immunological process, the host is the antibody and the guest the antigen.

The field of supramolecular chemistry was born with the synthesis of an azacrown ether namely dibenzo[18]crown-6. Other derivatives of crown ethers are also important this area. Like any other family of compounds, inserting other atoms (than oxygen) may improve the functionality of these compounds. Greene synthesized the first mono-azacrown ether (aza[18]crown-6) [9].

### III.RESULTS

A very good example of the supramolecular studies is the design, and synthesis of molecules, or metal complexes that can be used for the construction of sensing membranes that selectively response to a particular analyte, because of the incorporation of the designed species.

In such a case, it is necessary to match the size and binding properties of the species to make it or its derivative as selective towards the desired analyte as possible. The requirements for a potassium sensor, will as a result, be very different from one for a transition metal such as cobalt or even another alkali metal like sodium which is not very far from potassium both in the periodic table and from the aspect of chemical properties.

Likewise, a receptor molecule for tyrosine has different requirements, as compared to one for arginine, even though they are both amino acids. Matching of a receptor to an analyte may be considered an exercise in supramolecular chemistry.

Supramolecular chemistry is now a quite mature field and, hence the amount of information on molecular hosts and their affinities towards different guests in the scientific literature is considerable.



As a result, after searching the literature a scientist will be able to choose the best hosts for a specific analyte. [18]crown-6 ether is a good receptor for the protonated N-terminus of an amino acid and for the potassium cation. Therefore, it can function as a receptor for both of the above species.

Adding to the functionality of a host compound can make it more specific that is the mentioned host can be altered to have more affinity towards one of the mentioned target compounds as compared to the other. In the case of a potassium host, attachment of a short polyether side chain improves the binding, and can be achieved using an aza[18]crown-6 derivative.

On the other hand, the phenolic group in tyrosine will readily engage in  $\pi$ - $\pi$  interactions, so the incorporation of a substituent containing an aromatic group would give greater specificity for tyrosine. [10,11,12]

In general, the overall selectivity of the host guest interaction depends on factors such as:

- 1) The size of the cavity of the host should be large enough to accommodate the guest species. As the complexation happens, the hydration shell of the target species is removed and substituted by the donor atoms of the host (ligand).
- 2) The number of donor atoms in the ligand should be sufficient, to match the coordination number of the target species.
- 3) The flexibility of holding of donor atoms by the host backbone must be limited, so that their positions are suitable to match the shape of the coordination sphere of the target species.
- 4) Using the macrocyclic backbone, an excess of certain ligating groups can be avoided, thus improving the selectivity. For example in the case of a divalent cationic target two ionizable groups can be introduced into the host, which could hold more of them. The remaining two binding groups fill up the coordination sphere.
- 5) There is a possibility to attach chelating moieties onto host molecules, thus combining the chelate and the macrocyclic effect. However, the chelating groups increase the flexibility of the ligand and may reduce the overall selectivity.
- 6) Branched groups can be attached to proper sites of the host for high hydrophobicity and avoiding crystallized membrane phases.

Another requirement, for the application of supramolecular chemistry in building recognition devices is that the binding of the analyte to the receptor, or in other words the host guest interaction, must trigger an observable response through a reporter molecule.

The nature of the response will depend upon the analytical method used to detect the signal but will typically be colorimetric, electrochemical or fluorescent. An appropriate signaling mechanism may be designed to incorporate, for example, changes in conformation or molecular orbital energies that in turn affect the reporter molecule's electronic or spectroscopic signature upon analyte binding.

Finally, the receptor must be linked to the reporter molecule such that the effect of binding directly affects the latter without compromising the observable response. Sensors for the two analytes above could both be based on aza[18]crown-6 and contain a terminal anthracene group as a fluorescent reporter but differ in the link between them.

Not all of the supramolecular species, discussed above, have widespread applications in the construction of potentiometric ion selective electrodes. Because the aim of this review is to give an overall insight about the application of these compounds in the construction of ISEs, we will focus on the families of supramolecular compounds that are widely applied in the field of construction of sensors, in the following paragraphs. Hence, the classification in the following paragraphs will be different from that of the introduction.

Ion selective electrodes, being among the most favorable and fastest growing devices for chemical analysis, are well known to any analytical chemist or anyone concerned with chemical analyses [10]. These devices are well known for their applications in the fast, easy, cheap, and above all selective determination of ionic species in rather complex matrices. The rapid increase in the research and the consecutive reports on the design and construction of these devices is a practical proof of the great interest in these devices.

Ion selective sensors, as their name implies, are based on the selective recognition of one specific ion (target ion), as compared to the other ions that may be present with it. This so-called selective recognition is then converted to a potential signal, which is a measure of the activity of the target ion.

Many mechanisms have been suggested for the selective recognition of different ions in the electrodes [10], most of which focus on the selective complexation between the target ion and a specific species (the ion carrier or ionophore) that is incorporated in the liquid membrane of the electrodes, in order to create the desired selectivity.

Regarding what mentioned above, the selective complexation of target ions and ionophores, one may logically say that host guest chemistry, and in other words, the concept of supramolecular chemistry can be exploited in the design and construction of ion selective electrodes for different ionic species.

In the following paragraphs, we will try to review the history of application of the most well known supramolecular species in the field of potentiometric liquid membrane ion-selective sensors.

The structure of calixarene ligands to interact with cations, anions, neutral species and their various combinations, is determined by the character of other functional groups bonded to the basic skeleton of calixarenes. Another fascinating aspect of calixarenes is also their conformational variability and formation of stable and separable conformers with different reactivity and binding abilities. Structural and thermodynamics aspects of these changes have been studied NMR spectroscopy and X-ray crystallography.

Quantum mechanics and molecular dynamics are also used for the design of novel water-soluble calixarene ligands with effective ability to bind biologically important compounds like sugars, peptides, etc. [11-15]. Different calixarene based potentiometric liquid membrane ion sensors have been reported in the literature, which can be divided into the three groups of calixarene-based main group, transition metal, and lanthanide selective ion sensors.

In 1994, O'Connor et al, reported the complexing ability of 19 symmetrical, unsymmetrical and bridged calix[4]arene derivatives having ester, ketone, amide, amine and thio-ether functionalities by the picrate extraction method. They incorporated these calix[4]arene derivatives as neutral carrier ionophores in sodium-selective poly (vinyl chloride) membrane electrodes, and assessed their performance based on the sensitivity and selectivity over the alkali, alkaline earth metals and hydrogen and ammonium ions [16].

In the same year Y. Shibutani et al, studied six kinds of tetra alkylester type calix[4]arene derivatives, a diethyl-didecyl mixed ester, and three kinds of lower rim bridged which were characterized by electrochemical measurement to elucidate the effect of the length of the alkyl group of alkoxy carbonyl substituents on  $\text{Na}^+$  selectivity [17]. They found that to obtain excellent  $\text{Na}^+$  selective ionophores, introduction of short chain alkyl groups rather than long chain ones, such as a decyl group, and maintenance of sufficient solubility of the calix[4]arene derivatives in the membrane solvent are required concurrently. Among the calix[4]arenes tested, 25,26,27,28-tetrakis[(ethoxycarbonyl) methoxy]-p-tert-butylcalix[4]arene 2, and the diethyl-didecyl mixed ester type derivative 7 were the best ionophores for a  $\text{Na}^+$  selective electrode. On the other hand, sodium selectivity of the bridged type derivative 9 is comparable or even superior to that of the known bis(12-crown-4).

K. Kimura, Y. Tsujimura, and M. Yokoyama, reported the application of Silicone-rubber membrane sodium-ion sensors based on Calix[4]arene neutral carriers incorporating unsymmetrical structures and/or oligosiloxane moieties (which were highly dispersible in silicone rubber, and the application of these sensing membranes in ISFETs, in 1995 [18]. They increased the dispersibility of the ionophore by means of unsymmetrization. They claimed that these ion carriers realized high performance of silicon rubber-based sodium-ion sensors, i.e., high sensitivity, selectivity, and durability. They optimized the PVC/membranes to have a high  $\text{Na}^+$  selectivity against (especially with regard to  $\text{K}^+$  i.e.  $K_{\text{sel}} = 3.8 \times 10^{-3}$ ).

Neutral carriers, such as 16-crown-5 and calix[4]arene tetraester, immobilized on silicone-rubber membranes by covalent bonding were used to construct sodium ISFETs by Y. Tsujimura in 1996 [19]. The application of the calixarene ionophore together with an anion excluder exhibited high performance in terms of sensitivity, selectivity and response time.

T. Gardy et al, reported sodium-selective electrodes based on triester monoacid derivatives of p-tert-butylcalix[4]arene and compared them with tetraester calix[4]arene. All electrodes showed slopes in excess of  $50 \text{ mV dec}^{-1}$  ( $53.5\text{-}56.0 \text{ mV dec}^{-1}$ ) and lifetimes of at least 35 days. Virtually no difference in selectivity between the monoacid derivatives and the tetraesters was found. pH stability studies showed that the monoacid derivatives gave best performance at neutral pH, but at alkaline pH values (>8) there was a reduction in response, which did not occur with the tetraesters [13,14].

H. J. Lee et al reported All-solid-state sodium-selective electrodes based on room temperature vulcanizing-type silicone rubber matrix, and 1.0 wt percentage of tert-butyl calix[4]arene-tetraacetic acid tetraethyl ester [21]. In their work, they studied the effect of the used ionic additives, which were several phenyls; berate derivative-based additives, on the lifetime of the sensor. They found that membranes prepared with 0.5 wt % tetrakis[3,5-bis(trifluoromethyl)phenyl] berate salt (TFPB) exhibited low impedance, resulting in electrochemical performance comparable to that of the PVC-based membranes mounted in conventional electrodes. The lifetime of all-solid-state electrodes with tert-butyl calix[4]arene tetraethyl ester was longer than 230 days.

In 1998, Kimura et al reported the synthesis of an oligo(dimethylsiloxane) carrying ionophorous calixarene and applied it in the construction of sodium selective sensors, with a silicon rubber polymeric matrix [22]. The membrane contained 10 wt% of the ion carrier, which is equivalent to 4-6 wt% of the calix[4]arene unit.

Several works were reported on the Cs<sup>+</sup>-selective ionophores of this type in the year 2001. S. H. Lee et al, reported phenylene bridged calix[6]arenes for cesium selective ionophores [28]. K. C. Nam et al, studied the Synthesis and ion-binding properties of cesium selective quadruply bridged calix[6]arenes [29]. They prepared several quadruply bridged calix[6]arenes in high yields, by the reaction of various 1,4-di-O-alkylated calix[6]arenes with 1,2,4,5-tetrakis-(bromomethyl)benzene in the presence of Cs<sub>2</sub>CO<sub>3</sub>. The alkali metal extraction study showed that these compounds show high selectivities toward Cs<sup>+</sup> among alkali metal cations. The cesium binding characteristics were investigated with H-1 NMR and UV spectroscopy. L. X. Chen et al, [30] reported two novel double flexible spacers bridged biscalix[4]arenes 25,25',27',27'-bis(1,3-dioxopropane)-bis(5,11,17,23-p-tert-tetrabutylcalix[4]arene-26,28-diol) and 25,25',27',27'-bis(1,4-dioxobutane)-bis(5,11,17,23-p-tert-tetrabutylcalix[4]arene-26,28-diol) and evaluated as cesium ion-selective ionophore in polymeric membrane electrodes. The electrodes all gave a good Nernstian response of 51 mV per decade for Cs<sup>+</sup> in the concentration range from 1 × 10<sup>-1</sup> to 1 × 10<sup>-5</sup> M and good selectivity. The potentiometric selectivity of Cs<sup>+</sup>-ISEs based on the two compounds was selective toward cesium ion over other alkali metal ions, alkaline-earth metal ions and NH<sub>4</sub><sup>+</sup>. E. M. Chio et al, reported new quadruply-bridged calix[6]arenes as cesium selective ionophores in poly(vinyl chloride) (PVC) membrane electrodes. PVC membranes were prepared with dioctyl sebacate (DOS) or 2-nitrophenyl octyl ether (o-NPOE) as the solvent mediator and potassium tetrakis(p-chlorophenyl)borate as the lipophilic salt additive. These ionophores produced electrodes with near-Nernstian slopes. The selectivity coefficients for cesium ion with respect to alkali, alkaline earth and ammonium ions have been determined. The lowest detection limit (log a(Cs<sup>+</sup>) = -6.3) and the higher selectivity coefficient (log K(Cs<sup>+</sup>,Rb<sup>+</sup>)(pot) = -2.1 by SSM, -2.3 by FIM for calix[6]arene for Cs<sup>+</sup> have been obtained for membranes containing quadruply-bridged calix[6]arenes, which have no para t-butyl substituents on the bridging benzene ring [31].

#### IV. CONCLUSION

In 2002, S. W. Ko et al, reported Synthesis, structure and cesium binding properties of calix[6]arene biscrown, and its application as a cesium selective ionophore [32]. R. K. Mahajan reported a cesium ion selective electrode based on calix[4]crown ether-ester, in the same year [33]. The electrode was found to have selectivity for cesium ion over alkali, alkaline and transition metals. The electrode exhibited a good response for cesium ion over wide concentration range of 5.0 × 10<sup>-6</sup>-1.0 × 10<sup>-1</sup> M with a Nernstian slope of 59 mV per decade. The detection limit of electrode is 5.0 × 10<sup>-6</sup> M. The response time of the electrode is less than 20 s and can be used for more than 4 months without observing any divergence in potentiometric response.

In 2003, V. Arora et al, reported the synthesis of a new cesium selective calix[4]arene based chromoionophore [34]. They reported a novel azo-pyridyl calix[4]arene, (5,11,17,23-tetrakis(4'-azopyridyl)-25,26,27,28-tetrahydroxycalix[4]arene), in the 1,3-alternate conformations by coupling debutylated calix[4]arene with a diazotized solution of 4-aminopyridine. The selectivity coefficients for Cr<sup>3+</sup> and Ni<sup>2+</sup> was determined to be pK-Cr<sup>3+</sup>, Cs<sup>+</sup> = 6.6 and pK-Ni<sup>2+</sup>, Cs<sup>+</sup> = 66, while other alkali and alkaline earth metal ions do not interfere. S. W. Jeon et al, reported novel cesium-selective electrodes based on lipophilic 1,3-bisbridged cofacial-calix[6]crowns in 2004 [35]. They investigated five bis-bridged calix[6]crowns as Cs<sup>+</sup> ionophore in PVC membrane electrodes. Three 1,3-bisbridged calix[6]crown-4-ethers(I-III), 1,3-bisbridged calix[6]crown-5-ether(IV), and 1,3-bisbridged calix[6]crown-6-ether(V) were evaluated as ionophores. The membranes all gave good Nernstian response in the concentration range from 1 × 10<sup>-7</sup> to 1 × 10<sup>-1</sup> M of cesium ion. The best detection limits (-log a(Cs<sup>+</sup>) = 7.08-7.36) were obtained for electrode membranes containing 1,3-bisbridged cofacial-calix[6]crown-4-ethers, and the values are the lowest compared with those reported previously. The highest selectivity coefficients [pKCs<sup>+</sup> = 5.53(Cs/Na), 3.74(Cs/K), 2.63(Cs/Rb)] were obtained for the membrane of 1,3-bisbridged calix[6]crown-4-ether, and these values are also the highest compared with previous reports for Cs<sup>+</sup>-ISEs. The highest selectivity towards cesium ion was attributed to the geometrically co-facial positions of two crown-ethers in calix[6]crowns in order to provide the complex of cesium ion and eight oxygen atoms of cofacial crowns.

In 2003, Setsuko Yajima et al reported that calix[4]arene derivatives incorporating ω-unsaturated alkenyl groups or saturated alkyl groups and their monomeric analogues could be used as π-coordinate neutral carriers for ion-selective electrodes (ISEs) of soft metals [silver and thallium(I)] ions [36]. This can be considered as the continuation of their work in 1999. They reported A remarkable thallium(I) selectivity for ion sensors based on π-coordination of calix[4]arene neutral carriers, where calix[4]arene derivatives without any t-butyl group at the upper rim, such as calix[4]arene tetra(propyl ether) and tetra(allyl ether), were observed to provide the thallium(I)-selective electrodes with high sensitivity and ion selectivity. t-butylcalix[4]arene derivatives employed did not afford very good results as for the thallium(I) neutral carrier [37]. [15,16] Of course the work of Kyeong Soon Park et al, on thallium(I) selective

electrodes based on meso-alkyl substituted calix[4]pyrroles such as, meso-octamethyl-calix[4]pyrrole, meso-octaethylcalix[4]pyrrole and meso-tetraspirocyclohexyl-calix[4]pyrrole as sensor molecules in 2003, can also be regarded in this respect. The conditioned electrode incorporating meso-tetraspirocyclohexylcalix[4]pyrrole gave the best results with a wide working concentration range of  $10^{-5}$ – $10^{-1}$  M with near-Nernstian slope of 56.0 mV/decade of activity and detection limit of  $10^{-6}$  M. This electrode exhibited a fast response time of 30 s and high selectivity over  $\text{Na}^+$ ,  $\text{K}^+$  and other metal ions with only  $\text{Ag}^+$  interfering. The electrode worked well in a pH range of 2.0–11.0, and it could be successfully used in the determination of  $\text{Tl}^+$ [17]

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