DETERMINATION OF STABILITY CONSTANT FOR DIFFERENT METAL IONS USING SANDWICH MEMBRANE METHOD

A
Thesis Submitted
In partial fulfillments of requirements for the degree of

Master of Science in Chemistry

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CANDIDATE'S DECLARATION

I, hereby, declare that the work being presented in the thesis entitled **"DETERMINATION OF STABILITY CONSTANTS FOR DIFFERENT METAL IONS USING SANDWICH MEMBRANE METHOD"** in partial fulfillment of the requirements for the award of the degree of Master of Science in Chemistry, School of Chemistry and Biochemistry, Thapar University Patiala, is my own work during the period of Jan 2009 to May 2009, under the supervision of Professor Susheel Mittal and Dr. Sameena Mehtab, School of Chemistry and Biochemistry, Thapar University, Patiala. I have not submitted the matter embodied in this thesis for the award of any other degree.

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CERTIFICATE

This is to certify that the thesis entitled **"DETERMINATION OF STABILITY CONSTANTS FOR DIFFERENT METAL IONS USING SANDWICH MEMBRANE METHOD"**, being submitted by Mr. Ravinder Kumar in partial fulfillment of the requirements for the award of degree of Master of Science in the School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonifide work carried out under the supervision of Prof. Susheel Mittal and Dr. Sameena Mehtab and that no part of this thesis has been submitted for the award of any other degree.

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Contents

Abstract

A segmented sandwich membrane method is used to determine complex stability constants of two thiuram ionophores in solvent polymeric sensing membranes. These ionophores are commonly used in potentiometric and optical sensors, and knowledge of such binding information is important for ionophore and sensor design. In this method, two membrane segments are fused together, with only one containing the ionophore, to give a concentration-polarized sandwich membrane. Unlike other approaches, this method does not require the use of a reference ion in the sample and/or a second ionophore in the membrane, and is typically pH insensitive. The two ionophores TMTMS and TMTDS responsive for the cations copper and aluminium ions are characterized and discussed. The logarithmic complex stability constant 6.79 for Cu^{2+} and 6.65 for Al^{3+} are find out be the maximum among all the metal ions analysed. From the observed complex stability constants, maximum possible selectivities are calculated that would be expected if interfering ions show no binding affinity to the ionophore, Each ionophore is characterized in poly(vinyl chloride) membranes plasticized with a polar (NPOE).

1. INTRODUCTION

Stability constants are well known tools for solution chemists, biochemists and chemists in general to help determine the properties of metal-ligand reactions in water and biological systems. Metals, like aluminum, are well known by name, and ligands are what the metals are attached to, such as "acetate" (acetic acid), or "aluminum acetate". In general terms, the stability constant of a metal complex can be calculated as follows: $K = [ML] / [M][L]$, where K is the stability constant (expressed as a logarithm); M is the amount of metal ion and L is the amount of a ligand such as acetate. The total concentration of metal C_M can be computed with specialized computation programs. The basic equation $C_M = [M] + [ML]$ with $[ML] = K [M] [L]$ becomes $C_M = [M] (1 + K [L])$; hence $[M] = C_M / (1 + K [L])$ shows that the concentration of M depends on the stability constant of the complex and free concentration of the ligand which is dependent upon corresponding pK and pH values.

Carrier-based ion-selective electrodes (ISEs) are used extensively for the direct selective detection of ionic species in complex samples. For this type of electrodes, the stability constant of the ion–ionophore complex within the membrane phase is a very important Parameter that dictates the practical selectivity of the sensor. The sandwich membrane is the membrane made by pressing two individual membranes (ordinarily one without ionophore and one with the same components and an additional ionophore) together immediately after blotting them individually dry with tissue paper.

For the simple case of equal charge of the primary and interfering ion and equal stoichiometry of their complexes, the selectivity coefficient is an equilibrium constant and independent of the membrane concentrations of ionophore and lipophilic ionic sites, as long as the ionophore is present in excess relative to the sites. The observed selectivity is then directly proportional to the ratio of the stability constants of the involved complexes. But in this case, the relationship between selectivity and complex stability constants is also dependent on the concentrations of the relevant membrane components, and mathematical expressions are available that relate these parameters to each other for membrane optimization purposes.

A number of methods are today available to measure ion – ionophore stability constants. *Like* spectrophotometric method on thin plasticized poly (vinyl chloride) (PVC) films was used to determine the apparent complex stability constants of ion carriers directly within the polymeric phase. An analogous potentiometric method to determine effective complex formation constants in the organic membrane phase was reported as well. The two methods do have some drawbacks. First, the HC-selective ionophores may not behave ideally in membrane matrices. Second, careful pH control is required. Since a large number of ions are only soluble within a limited pH window, it limits the application of these methods. Third, these methods cannot be used for anion-selective and electrically charged ionophores. Complex stability constants have also been determined with voltammetric experiments at liquid–liquid interfaces. While voltammetry is intrinsically a kinetic method, and therefore, perhaps less reliable than potentiometry in this respect, no rigorous study has been performed so far to show whether voltammetry is a truly viable alternative.

An excellent correlation was found to complex stability constants observed with the two previously mentioned methods. It is more widely applicable since no careful pH control is required. The method was originally proposed by Mokrov *et al.,* for ordinary ion selective electrode membranes that show no interferences from other sample ions, the membrane potential is independent of the incorporated ionophore since the concentration changes at both interfaces are symmetrical. In this method, the two phase boundary potentials are uncoupled from each other by fusing two membranes, with only one containing the ionophore, to form a sandwich. If both contacting aqueous solutions have identical composition, the initial membrane potential is a direct function of the activity ratio in both membrane segments. The ionophore will decrease the ion activity in one segment by orders of magnitude relative to the one that contains no ionophore. The measured potential difference of the sandwich membrane and a single membrane is, therefore, conveniently used to calculate the complex stability constant. This method does not require a reference ion or second ionophore, which makes the resulting formation constants less likely biased from other experimental artifacts.

Thiuram ionophores

The two ionophores Tetramethylthiurammonosulphide (TMTMS) Fig. 1 and Tetraethylthiuramdisulphide (TETDS) Fig. 2 are used in these studies. Thiram is a dimethyl dithiocarbamate compound used as a fungicide to prevent crop damage in the field and to protect harvested crops from deterioration in storage or transport. Horsfall *et al.,* was the proposed that the fungicidal effect of thiram was connected with their ability to form complexes with the heavy metal ions. It was observed that fungitoxicity of TMTDS was not reversed by addition to the medium of the trace metals Fe, Zn, Cu, Mn and Mo. Thiram is slightly toxic by ingestion and inhalation but it is moderately toxic by dermal absorption. Thiram is irritating to the eyes, skin, and respiratory tract. It is a skin sensitizer. Thiram was not found to be carcinogenic. Thiuram sulfides in a suitable organic solvent can be used to extract metal ions selectively. Mendoza *et al.*, found out that silver(I) was perfectly extracted with TMTMS Fig. 3.

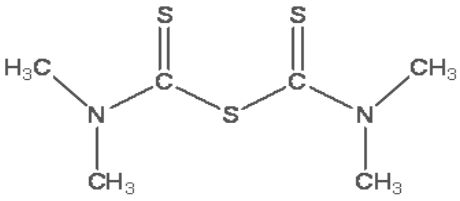

Fig. 1 Structure of Tetramethylthiurammonosulphide (TMTMS) ionophore

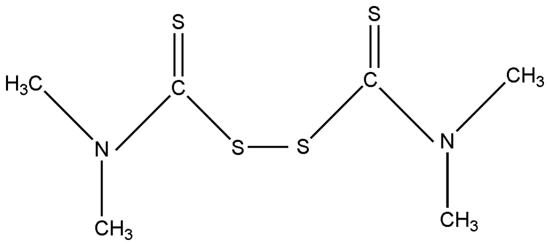

Fig. 2 Structure of Tetraethylthiuramdisulphide (TETDS) ionophore

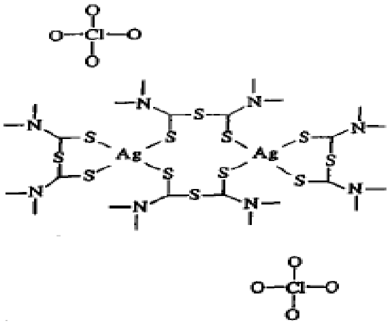

Fig. 3 Crystal Structure of Bis(N,N,N,N-tetramethylthiurammonosulfide)silver(I) Perchlorate

A similar coordination of the thiuram monosulfide was found in iodo (dipentamethylenethiurammonosulfide) copper(II). The structure of $[Ag\{(CH_3)_4(CN)_2\ S_3\}_2]^+$ is a centrosymmetric binuclear complex, which exhibits a distorted tetrahedral coordination geometry about the silver atom. The silver atoms are in coordination with the two sulfur donor atoms of one TMTMS molecule and by two of the sulfur atoms of two other bridging TMTMS molecules. The tetrahedral distortion at the silver arises partly from molecular packing as well as other sterical reasons; especially the methylene groups have a pushing effect on the S_3 atom which makes the S_1-Ag-S_3 angle bigger than the other angles. Based on the sum of the expected tetrahedral single-bond covalent radii of 2.56 Å, it is quite clear that the Ag-S bonds in $[Ag\{(CH3)_4(CN)_2S_3\}_2]$ $[ClO_4]$ are fairly covalent. In this work, the structure of the complex formation between Ag(I) and tetramethylthiuram monosulfide in the presence of a perchlorate counter ion was clarified. It thus seemed interesting to investigate a mercury complex of the TETDS in order to study the mode of its coordination to silver. Ag(I) and Hg(II) both have d^{10} electrons, and have approximately the same ionic and tetrahedral covalent radii.

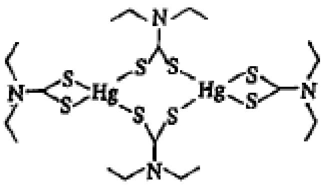

Fig. 4 Crystal Structure of Bis(N,N-diethyldithiocarbamate)mercury(II)

The structure consists of binuclear complexes with a center of symmetry. Each Hg atom is situated in a highly distorted environment coordinated by two S consistent with double-bond character in this linkage Fig. 4. This complex was found to be isomorphous to $Zn[(CH_3)_2NCS_2]_2$ and $Cd[(CH_3CH_2)_2NCS_2]_2$.

Thiram has been formulated for use as dusts, wettable powders and flowable suspensions and also in combination with other pesticides. Griepentrog *et al.* reported that these are effective against mice, guinea pigs as allergenic sensitization agent. Thiram has been used in the polyolefin industry as an oxidant and as a peptizing agent in polysulfide elastomers. Thiram is also used as a seed protectant and to protect fruit, vegetable, ornamental and turf crops from a variety of fungal diseases. In addition, it is used as an animal repellent to protect fruit trees and ornamentals from damage by rabbits, rodents, and deer. Thiram is available as dust, flowable, wettable powder, water dispersible granules, and water suspension formulations, and in mixtures with other fungicides. Thiram has been used in the treatment of human scabies, as a sunscreen and as a bactericide applied directly to the skin or incorporated into soap. Thiram is also used as an accelerator and vulcanization agent in the rubber industry. It has been in commercial use since 1925. Thiram is also an environmental degradation product of the two fungicides, ferbam and ziram. Thiram is typically sold as a fungicide.

Objective:

The purpose of the present work will be:

- To select some commercially available neutral carriers.
- To prepare metal-ligand complexes with alkali, alkaline earth and transition metal ions.
- To develop carrier based ion-selective membranes by incorporating these ligands into suitable matrix like PVC or Polystyrene.
- To Screen out the characteristics of these membranes for optimum sensitivity and determination of the stability constant of these metal ions with ionophores.

2. LITERATURE SURVEY

Molecular associations between a receptor or host molecule (ionophores) and a substrate or guest molecule (metal ion) to form metal ligand complexes have been widely recognized and studied since a long time ago and different techniques have been investigated to determine the stability constant.

Gupta *et al.,* (2008) reported a fabrication of new potentiometric alizarin sensor based on the use of alizarin Red-S-CTAB ion pair, in poly (vinyl chloride) (PVC) matrix. It was successfully applied to determination of vanadium ion in water and soil samples, zirconium ion in alloy samples and molybdenum ion in geological samples. In 2009 they also prepared a new highly selective terbium(III) electrode with a polymeric film doped using 2-benzothiazolyl-2-amino-α-(methoxyimino)-4-thiazolethiol acetate as an electroactive material, benzyl acetate (BA) as a plasticizer, and potassium tetrakis(4-chlorophenyl) borate as an anionic site.

Singh *et al.,* (2008) prepared Plasticized membranes using 3-(2-pyridinyl)-2H-pyrido[1,2,-a]-1,3,5-triazine-2,4 (3H)-dithione (L_1) and acetoacetanilide (L_2) and explored as Cu^{2+} selective sensors.

Jeong *et al*., (2006) use Polymeric Iodide-ion Selective Electrodes Based on Urea Derivative as an Ionophore. The proposed electrode showed good selectivity and response for iodide anion over a wide variety of other anions in pH 5.0 buffer solutions.

Ganjali *et al*., (2005) presents a new ionophore of novel calcium sensor based on [2-(2-hydroxyphenyl)imino]-1,2-diphenylethanone, in this work, a novel calcium pvc-based membrane sensor based on 2-[(2-hydroxyphenyl)imino]-1,2-diphenylethanone (HD) as a new ionophore is presented. They determine stability constant for alkali and alkaline earth, and some mono, di and trivalent cations, such as Li^+, Na^+, K^+, Mg^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, Cu^{2+}, Al^{3+}, La^{3+} and Ce^{3+} ions.

Ganjali *et al.,* (2006) prepared a novel Pr(III)-selective membrane sensor based on *N*-(pyridin-2-ylmethylene)benzohydrazide (PBA). The plasticized membrane sensor exhibits a Nernstian response for Pr(III) ions over a relatively wide concentration range (1.0×10^{-2} to 1.0×10^{-6} M) with a limit of detection of 8.0×10^{-7} M (115 ppb). It has a fast response time of 20 s and can be used for at least 6 weeks without observing any major deviation. They also described 2006 in a novel potentiometric membrane Eu(III) ion sensor based on a new S–N hexadentates Schiff's base, bis(thiophenol)butane2,3-dihydrazone (SNSB). The sensor exhibited a Nernstian response over a concentration range of 1.0×10^{-5} to 1.0×10^{-2} M, with a detection limit of 5.0×10^{-6} M.

Saleh *et al*., (2005) prepared and studied an ion-selective PVC membrane sensor for cerium(III) ions based on [4-(4-nitrobenzyl)-1-phenyl-3,5-pyrazolidinedion)] (NBPP). This electrode has a wide linear dynamic range from 10^{-1} to 2.5×10^{-6} mol L^{-1} with a Nernstian slope of 19.5 ± 0.2 mV decade^{-1} and low detection limit of 1.6×10^{-6} mol $^{-1}$. It has a fast response time (<10 s) and good selectivity with respect to different metal ions.

Pietrzak. *et al*., (2007) examined aluminum(III) and zirconium(IV)-tetra phenyl porhyrin (TPP) derivatives as fluoride selective ionophores for preparing polymer membrane-based ion-selective electrodes (ISEs). The anion binding stability constants of the ionophores are characterized by the so-called "sandwich membrane" method.

Bakker and Chumbimuni-Torres (2008) gives an overview of the newest developments of polymeric membrane ion-selective electrodes. Which gives the electromotive force may be used to assess binding constants of the ionophore, and how the selectivity and detection limit are related to the basic membrane processes. Again Bakker *et al*.,(1998) determined complex formation constants of neutral cation-selective ionophores in solvent polymeric membranes with the use of spectrophotometric measurements. He found experimental results with the ionophores valinomycin and BME-44 (for K^+), ETH 4120 (for Na^+), ETH 1001 and ETH 129 (for Ca^{2+}), and ETH 7025 (for Mg^{2+}). Yanming and Bakker., (2000) used segmented sandwich membrane method to determine complex formation constants of 18 electrically neutral ionophores in solvent polymeric sensing membranes. He characterized each ionophore in poly(vinyl chloride) membranes plasticized either with a polar (NPOE) or a nonpolar plasticizer (DOS). Membranes based on npoe always show larger complex formation constants of the embedded ionophore.

Meloun and Bartos,(1988) determined the stability constants log *K,* of the acid H/L by regression analysis of potentiometric titration data when common parameters and group parameters are refined. The influence of three kinds of error on the protonation constants has been investigated: error from the strategy of minimization, random error, and error from uncertain estimates of group parameters.

3. THEORY

3.1 Ion-selective Electrodes

Ion-selective electrodes (ISEs) are electrochemical sensors that allow potentiometric determination of the activity of certain ions in the presence of other ions; the sample under test is usually an aqueous solution. Response of these sensors towards charged species is provided by ion-selective membranes, which can be prepared from different materials glass, solid crystalline, ceramic or polymers. Their selectivity can be achieved either by means of material structure or by doping the membrane with specific ion-selective complexing agents. Changes in the activity of certain ion in the sample cause changes of the membrane potential that is measured as ISE response against a reference electrode. Observation of potential arising between two electrodes under zero current conditions is an essence of potentiometry, which is a very simple and useful electro-analytical method. ISEs are applicable in a number of fields, such as clinical, environmental, and process monitoring, as well as more novel approaches such as microfluidic based systems and micro/nanoprobes. The most successful ISE is still probably the glass pH-electrode used whenever it is necessary to adjust or control pH in aqueous or organic media. On the other hand, comparing to solid crystalline, ceramic, and glass membrane ISEs, most widely employed are electrodes with polymer membranes. By using hundreds of different ionophores, now a days it is possible to measure up to 50 ions. Ionophore-based sensors currently provide robust, portable, simple, and relatively cheap method of analysis. They can be improved both by development of membrane constituents, electrode design, and by new methodologies of data acquisition and interpretation.

3.2 Membranes

A membrane is a phase, finite in space, which separates two other phases and exhibits individual resistance to the permeation of different species. Ion selective sensors generally employ homogeneous/heterogeneous membranes of chemical compounds. The capability to differentiate between various permeating species is the principal characteristics of a membrane used in electrochemical sensors. This differentiation leads to the formation of an electrical double layer, which is the source of electric potential. The potential developed is basically due to two processes: (i) different mobilities of the ions through the membrane resulting in the generation of diffusion potential, (ii) Donnan or phase boundary potential arising from non-transport of one or more type of ions. The potential developed is a function of activity ratios of the exchangeable ions on the two sides of the membrane.

The membrane can play a critical role in the performance of the sensor in a particular environment. A successful membrane needs to be generally hydrophobic, have ion-exchanger properties and contain a lipophilic ionophore that provides selectivity to the sensor. The lack of ion-exchanger properties would lead to substantial uptake of sample cations as well as anions into the membrane, leading to effective breakdown of so-called perm selective behavior.

3.3 Membrane Materials

In general, the polymeric membrane used in ISEs consists of four components: Electroactive material (ionophore), lipophilic additive, plasticizer and the polymer matrix.

3.3.1 Electroactive material (ionophore)

Ionophore, or ion carrier, or ligand is the key components of polymeric membrane ion-selective electrodes that govern the ion selectivity and sensitivity because the molecular-level phenomenon, sensed by the ISE is the binding between the ionophore and target ion. Ideally, it forms reversible and relatively strong complex with target ion and not with the other ions. There are two kinds of ionophore, charged and neutral carrier. Various substances *viz*. inorganic and organic ion exchanger, solid electrolyte, salts of multivalent atoms, metal chelates, polyaza, polythia macrocycles, crown ethers, cryptands and calixarenes have been used as ion carriers for the preparation of ISEs. To be used as suitable ion carrier; the active sensor material should be physically compatible with the matrix, have a low solubility product, must exhibit some electrical conductivity, have balance between the free energies of ion-ligand interaction, ion-hydration and undergo rapid ion exchange at the membrane sample interface. In order to keep the membrane composition constant, the ionophore must retain within the membrane; therefore, aside from the binding centre it must contain numerous lipophilic groups. From a more mechanistic perspective, the potentiometric response of membrane-based ISEs containing a specific ionophore can be used to provide information about the mode of analyte binding as well as, at least potentially, molecular insights into the details of the relevant substrate receptor interactions.

3.3.2 Polymeric (inert) matrix

The matrix provides an inert base that imparts physical-mechanical stability and elasticity to the membrane. Polymer matrix is chemically inert, hydrophobic, tough, flexible, non-porous, crack resistant and should not swell in sample solutions. Silicon rubber, some methacrylates polyurethanes and polystyrene, polyamide or polyimide have been demonstrated as polymer matrices meeting this requirement, while the most commonly used polymer is poly (vinyl chloride) (PVC) due to simplicity of membrane preparation. Of the various binders used for preparing heterogeneous solid state membranes, PVC has been most widely used due to its relatively cheap cost, good mechanical properties, inertness and amenability to plasticization.

It also offers good resilience to mechanical and pressure damage. Electroactive materials are highly compatible with the matrix, reduced leaching from the membrane and increased in electrode life to a substantial extent. Thomas and Moody are the pioneers in developing PVC based electrodes. Thomas *et al.* in 1986 recommended PVC as the most significant polymer support.

3.3.3 Solvent mediator or plasticizer

The plasticizer to be used in membranes should exhibit high lipophilicity, high molecular weight, low tendency for exudation from the polymer matrix, low vapor pressure and high capacity to dissolve the substrate and other additives present in the membrane. It is well documented that the addition of plasticizers not only improves the workability of the membranes but also contributes significantly towards the improvement in the detection limit, stability and shelf life of the sensor. Additionally, its viscosity and dielectric constant should be adequate. It enhances the flexibility and softness of the fabricated membrane and provides mobility of membrane constituents within the membrane phase. Being a dominating component of PVC membranes, plasticizer acts as a membrane solvent, affecting membrane selectivity through both extraction of ions into organic phase and influencing their complexation with the ionophore.

In order to obtain a homogeneous organic phase, plasticizer must be compatible with the polymer and other membrane constituents have to be soluble in it. Polymeric membrane usually comprises of a matrix containing *ca.* 33 % (w/w) of PVC and 66 % of (w/w) solvent mediator. A number of organic solvents such as phthalates, sebacates, octyl ethers, acetophenone and benzyl acetate have been suitably and efficiently used as plasticizer to enhance the performance of ISEs.

3.3.4 Lipophilic additive or lipophilic ionic sites

The prerequisite for obtaining a theoretical response with ISE membranes is their perm-selectivity, which means that no significant amount of counter ions may enter the membrane phase. Lipophilic ionic additive is a salt of non-exchangeable lipophilic anion/cation and an exchangeable counter ion. Their main function is to render the ion selective membrane perm selective, to optimize sensing selectivity (by defining the ratio of complexed to uncomplexed ionophore concentration in the membrane) and to reduce the bulk membrane impedance. The presence of lipophilic additive in ion selective membrane electrodes not only diminish the ohmic resistance and enhance the behavior but also in cases where the extraction capability is poor, increase the sensitivity of membrane electrodes. These additives may also catalyze the exchange kinetics at the sample membrane interface.

Although the presence of the ionic sites is mandatory, membranes may function without deliberately incorporated ionic sites because of impurities in the polymer matrix or in other components. Their concentration relative to the ionophore has an important selectivity modifying effect due to the influence of the involved equilibrium. Various tetraphenylborate derivatives are currently used as anionic additives while tetraalkylammonium salts are used as cationic additives. The charge of the proper additive is tied directly to the response mechanism of the chosen ionophore.

3.4 Segmented Sandwich Membrane Method

Segmented sandwich membrane method consists in the direct measurement of potential contribution arising from the ligand-ion complexation. Two membranes, one containing ion exchanger only and another containing exactly the same amount of ion exchanger and ionophore are bathed symmetrically in identical solutions. Two kinds of ISEs with conditioned membranes are prepared and their potentials are examined under symmetrical conditions i.e., inner filling solutions (IFS) and sample solutions are the same as one used for membrane conditioning. Under symmetrical conditions the membrane potential, E_M, is zero so that the observed potential of ISE corresponds to the sum of the constant potential contributions, represented in the Nernst equation by E_0.

Fusion of ion exchanger based membrane with that containing ionophore results in a segmented sandwich membrane with two different phase boundaries. On one of them potential is dictated by ion exchange (E_0), while on the other additionally by ion-ionophore complexation (E_M). Sum of their potentials, Esw, is measured as response of ISE with segmented sandwich membrane and the phase boundary potential E_M, related to the ion-ionophore reaction, is used for calculation of the effective complex formation constant.

Further development of this elegant method allowed determination of the coextraction constants, so that knowing it and effective complex formation constant, it is now possible to predict upper and lower detection limits of ISE. Segmented sandwich membrane technique was also used for quantification of the ionic impurities in polymeric ISE membranes. A recently published new titration technique applied for segmented sandwich membrane method allows determination of ion-ionophore complex stoichiometry.

3.5 Preparation of Membranes

3.5.1 Preparation of poly(vinyl chloride) based membranes

Of the various binders used for preparing heterogeneous solid-state membranes, PVC has been most widely used due to its relatively cheap cost, good mechanical properties, inertness and amenability to plasticization. An important requirement for making PVC membranes of a neutral ionophore is that the ionophore, PVC and plasticizers should be soluble in some fast evaporating solvent. Therefore, the membranes were prepared by dissolving different amounts of ionophore, PVC, plasticizer and ion excluder in THF. After thorough dissolution, the homogeneous mixture was concentrated by evaporating THF and it was then poured into polyacrylates rings placed on a smooth glass plate. The solution should be poured gently so that bubbles could not form. After the evaporation of THF, a transparent membrane of was formed and it was removed carefully from the glass plate and glued to one end of Pyrex glass tube.

Besides the critical role of the nature of ionophore in preparing membrane-selective sensors, some other important features of the PVC based membrane electrode, such as amount of ionophore, nature of solvent mediator, plasticizer/PVC ratio and nature of additive used are known to significantly influence the sensitivity and selectivity. Thus, the ratio of membrane ingredients, time of contact and concentration of equilibrating solution *etc.* were optimized after a good deal of experimentation to provide membranes, which generated reproducible and stable potentials. The blank membrane having only PVC as membrane ingredients was also prepared to observe whether any background potentials were generated or not.

3.5.2 Preparation of sandwich membranes

Ion-selective electrode membranes were cast from above mentioned procedure. The blank membranes (without ionophore) were also prepared having same composition. The sandwich membrane was made by pressing two individual membranes (ordinarily one without ionophore and one with the same components and an additional ionophore) together immediately after blotting them individually dry with tissue paper. The obtained sandwich membrane was visibly checked for air bubbles before mounting in electrode body with the ionophore-containing segment facing the sample solution. The combined segmented membrane was then rapidly mounted on to the electrode body and measured immediately.

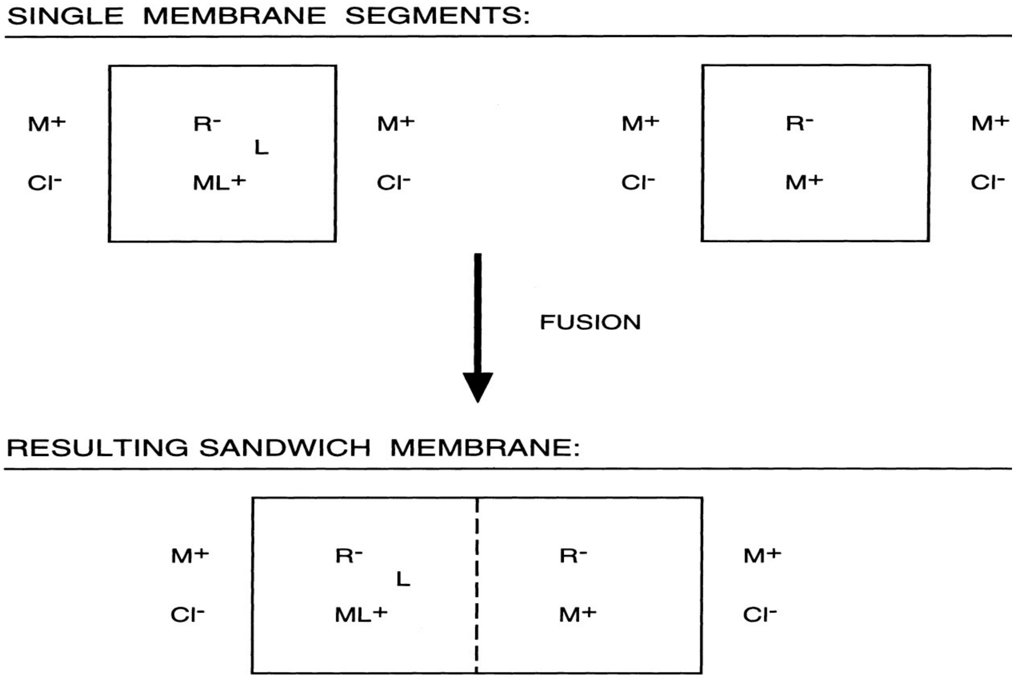

Fig. 5 Schematic presentation of the potentiometric two-layer sandwich membrane method to determine complex formation constants in solvent polymeric membranes. The resulting membrane is concentration polarized and contains only on one side the lipophilic ionophore. A membrane potential measurement of this transient condition reveals the ion activity ratio at both interfaces, which translates into the apparent binding constants of the ion–ionophore complex.

3.6 Determination of stability Constant

A selective complexation of analyte ions by ionophores is primarily responsible for the selectivity of sensors. Despite the wide use of lipophilic and chemically immobilized ionophores in chemical sensor applications, only a limited number of experimental techniques are available to assess the binding strengths of these highly selective molecular probes directly in the polymeric matrix of the sensor. A different approach to measure complex stability constants in ISE membranes relies on recording electrical potential of segmented sandwich membranes Qin *et al*., Polymeric membrane electrodes primarily respond to ion activities on both sides of the aqueous-organic phase boundary. The incorporation of an ion carrier into the membrane phase should induce a substantial potential change at the sample-membrane phase boundary, since the ion activity within the organic phase is dramatically altered. Therefore this effect could be used to determine the formation constant of the ion-ionophore complex.

In present studies the stability constants are investigated according to method proposed by Mi and Bakker (1999) using following equation

$$\beta_{IL_n} = \left(L_T - \frac{nR_T}{Z_I} \right)^{-n} \exp\left(\frac{E_M z_I F}{RT} \right)$$

Where L_T is the total concentration of ionophore in the membrane segment, R_T is the concentration of lipophilic ionic site additives, n is the ion-ionophore complex stoichiometry and R, T and F are the gas constant, the absolute temperature and the Faraday constant respectively and an ion carries a charge of z_I-. This relationship allows for the convenient determination of formation constants of ion-ionophore complexes within the membrane phase on the basis of transient membrane potential measurements on two-layer sandwich membranes. The knowledge of formation constants of the relevant complexes is beneficial to the process of optimizing the structure of ionophores and the composition of ISE membranes for given analyte ions.

3.7 Combination Electrode/Cell Assembly

It is an electrochemical apparatus that incorporates an ion-selective electrode and a reference electrode in a single assembly, thereby avoiding the need for a separate reference electrode.

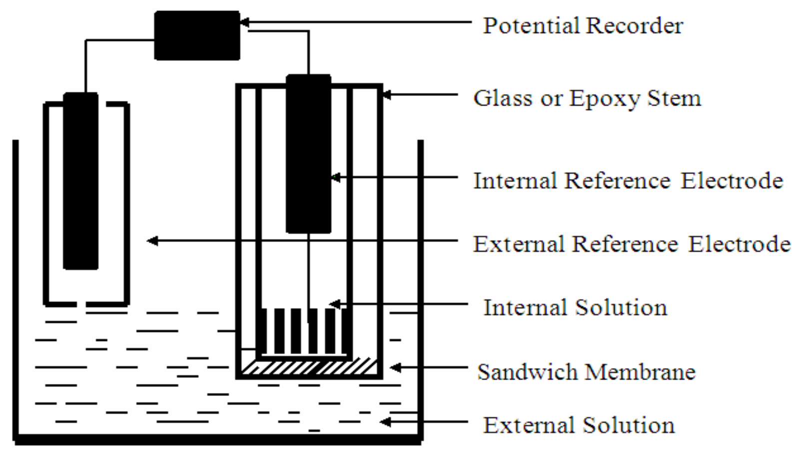

Fig. 6 Assembly for determination of potential across sandwich membrane

It requires membrane potential measurements on two-layer sandwich membranes, where only one side contains the ionophore. If both membrane segments have the same ionic strength, it is convenient to assume that the activity coefficients for the complexed and uncomplexed ions are approximately equal. In that case, they can be omitted and the complex constant is related to the potential.

3.8 To Find Metal-Ligand Stochiometry (Mole Ratio Method)

Perhaps the simplest of the spectrophotometric techniques that have been used for the study of complex formation equilibria is the molar ratio method. A series of solutions are prepared which contain equal formal concentrations of a metal ion but different formal concentrations of the complexing agent. The ratio of these concentrations should usually vary from about 0.1 to 10 or 20. The absorbance of each solution is then measured. If only the complex absorbs at the wavelength where measurements are taken then these absorbance's are proportional to the equilibrium concentrations of the complex ion in the solutions, and a plot of the absorbance against the ratio of the number of moles of ligand to the number of moles of metal ion (which is the same as the ratio of the corresponding total or formal concentrations).

The method is analogous to a spectrophotometric titration if one plots the absorbance, corrected for dilution, against the ratio of the number of moles of the ligand to metal ion. Note that, as in a spectrophotometric titration, this method yields results if the ligand or metal ion absorbs at the wavelength used for measurements but the shape of the curve is different. The extent of the curvature in the vicinity of the end point depends on the degree of dissociation of the complex. However, the stoichiometric formula of the complex can be found by extrapolating the straight-line portions of the graph, which is to say that the point at which these lines intersect corresponds directly to the ratio of ligand to metal ion in the complex. This procedure works very well for weakly dissociated (*i.e.* mostly associated) complexes. But if the dissociation constant of the complex is too large, the molar ratio plot will become a smooth continuous curve and it will be impossible to locate the stoichiometric point. In such cases, better results can often be secured by the slope-ratio or continuous-variations methods. Within a certain rather restricted range, however, the curvature around the "end point" of a molar ratio plot can be turned to good advantage and used for the calculation of the dissociation constant of the complex. Another advantage of the mole ratio method over the method of continuous variations is its increased accuracy in differentiating ML_5 vs. ML_6 type complexes.

4. EXPERIMENTAL

4.1 Reagents

Sodium tetraphenyl borate (NaTPB), o-nitrophenyloctylether (NPOE) was obtained from sigma Aldrich, high molecular weight PVC and tetrahydrofuran (THF). Ionophores TMTMS (tetramethylthyurammonosulphide) and TMTDS (Tetraethylthyuramdisulphide) were purchased from Fluka. Metal salts $Al(NO_3)_3$, CuN_2O_6, $Ni(NO_3)_2$, $Fe_3N_3O_9$, $Ca(NO_3)_2$, $Hg_2(NO_3)_2$ were purchased from Sigma-Aldrich, and $Zn(NO_3)_2$, $Pb(NO_3)_2$, from Sdfine and NaCl from Loba cam. And $AgNO_3$ were purchased from Qualizen. Aqueous solutions (0.1 M) were prepared by dissolving the appropriate salts in distilled water.

4.2 Electrode setup and EMF measurements

Ion selective electrode membranes were cast by dissolving the ionophore and NaTPB, together with PVC and the plasticizer *o*-NPOE to give a total cocktail mass of 106 mg, in 5 mL of THF and pouring it into a glass ring affixed with rubber bands onto a glass slide. The solvent THF was allowed to evaporate overnight. The ratio of membrane ingredients, were optimized and the best membrane composition is mention in Table 1. The parent membranes were then removed from the glass and conditioned overnight in appropriate solutions: 0.1 Molar nitrate solutions for the transition metal ions Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Hg^{+} and 0.1 chloride solution for alkali metal ion Na^{+} and 0.1 nitrate solution for alkaline earths Ca^{2+} and representative metal ions Al^{3+}, Pb^{2+}. All membrane electrode potential measurements were performed at laboratory ambient temperature in unstirred salt solutions (identical to the inner filling solution) versus a double junction reference electrode with a 1 M KNO_3 bridge electrolyte. The sandwich membrane was made by fusing two individual membranes (one without ionophore and one with the same components and additional ionophore together with pressure from a metal spatula, after blotting them individually dry with tissue paper. The obtained sandwich membrane was visibly checked for air bubbles before mounting in the same electrode body with the ionophore-containing segment facing the sample solution. The potential was recorded for five minute interval in the appropriate salt solution. The elapsed time between sandwich fusion and exposure to electrolyte was typically < 12 hours.

Table. 1 Optimized composition of various components for membrane preparation.

S.No.	Compound	Composition (mg)
1	Poly(vinyl)chloride	33
2	TMTMS / TETDS	4.0
3	2-Nitrophenyl octyl ether 99 %	67
4	Sodiumtetraphenylborate 99.5 %	2.0

4.3 Results and Discussion

In order to know the stochiometry of ligands with metal ion, in preliminary experiments tetramethylthiurammonosulphide (TMTMS) and tetraethylthiuramdisulphide (TETDS) were used as suitable ligands in spectrophotometric techniques for the study of complex formation equilibria by the molar ratio method. A series of solutions were prepared which contain equal formal concentrations of a metal ion and formal concentrations of the complexing agent. It was found that the ratio of the concentrations with various metal ions (stochiometry) was approximately 1:1. Variation of Absorbance v/s concentration of ligand/concentration of metal is presented in Figs. 7-10.

The composition of membrane with different plasticizers and additive, performing best is given along with their characteristics in Table 1. Among the three different plasticizers (NPOE, DBP, TBA), the NPOE is a more effective solvent mediator in preparing the selective membrane electrode. To investigate stability constants two different membrane with composition 4 mg Ionophore, 2 mg NaTPB, 67 mg NPOE and 33 mg PVC were prepare with TMTMS and TMTDS as ionophores. Experimental values of EMF for TMTMS and TETDS of PVC (blank) and sandwich membranes in mono, di and tripositive metal ion solution (0.1 M) are represented in Tables 2-4.

Among different tested cations, Cu^{2+} ion gives best stability constant (6.79) with TMTMS and Al^{3+} with TMTDS. The stability constant obtained for all other tested cation were much lower than these cupper and zinc ions. The determined formation constants ($\log \beta_{\mathrm{IL}n}$) for the examined cations were recorded in Table 5 and 6.

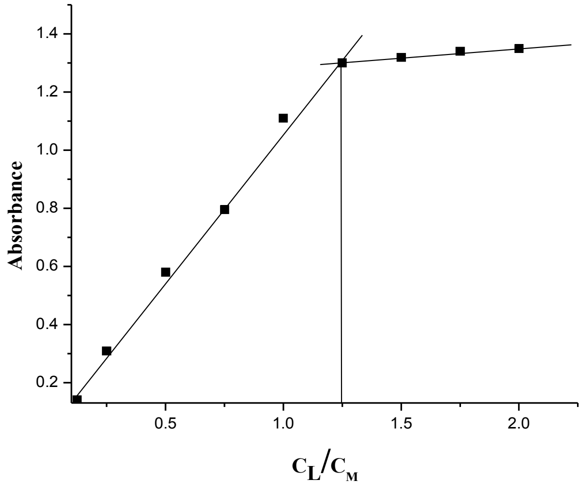

Fig. 7 Determination of stochiometry (1:1) between TMTMS with Ag^+ ion

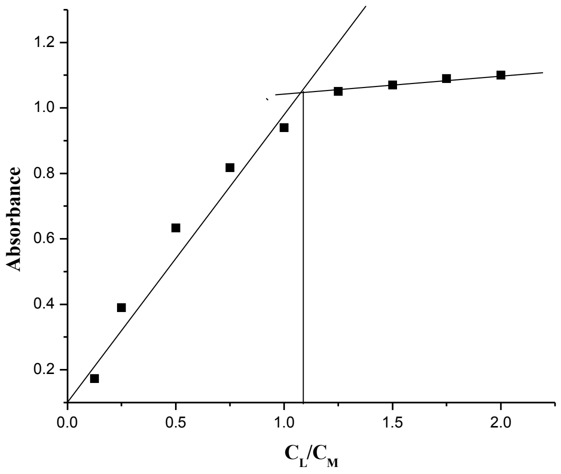

Fig. 8 Determination of stochiometry (1:1) between TMTMS with Cu^{2+} ion

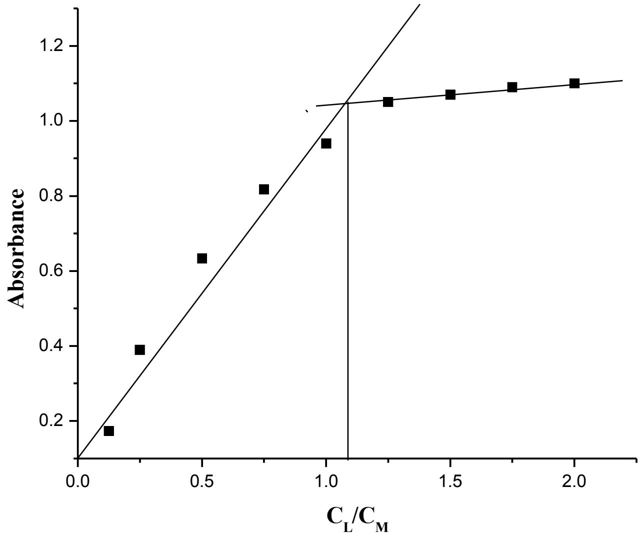

Fig. 9 Determination of stochiometry (1:1) between TMTMS with Al^{3+} ion

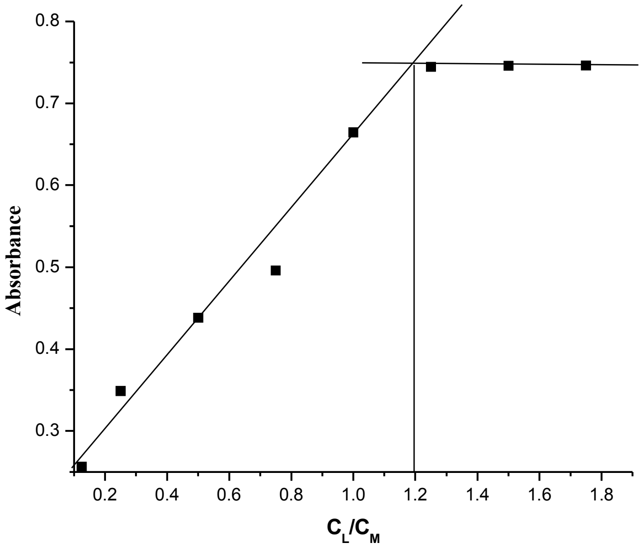

Fig. 10 Determination of stochiometry (1:1) between TETDS with Al^{3+} ion

Table. 2 Experimental values of EMF for TMTMS and TETDS for PVC (blank) and sandwich membranes in Ag^+ (0.1M) solution.

S. No.	Time (min)	EMF of PVC (Blank) Membrane in $AgNO_3$ (0.1 Molar)		EMF of Sandwich Membrane in $AgNO_3$(0.1 Molar)	
		For TMTMS	For TETDS	For TMTMS	For TETDS
1	0	-0.014	0.025	0.000	0.025
2	5	-0.012	0.035	0.004	0.029
3	10	-0.007	0.040	0.008	0.033
4	15	-0.005	0.045	0.011	0.038
5	20	**0.000**	0.047	0.013	0.043
6	25	0.000	0.049	0.015	0.048
7	30	0.000	0.050	0.016	0.053
8	35	0.000	0.051	0.017	0.058
9	40	0.000	**0.052**	0.018	0.063
10	45	0.000	0.052	0.019	0.068
11	50	0.000	0.052	0.019	0.072
12	55	0.000	0.052	**0.020**	**0.076**

Table. 3 Experimental values of EMF for TMTMS and TETDS for PVC (blank) and sandwich membranes in Cu^{2+} (0.1 M) solution.

S.No	Time(min)	EMF of PVC(Blank) Membrane in Cu $(NO_3)_2$ (0.1 M)		EMF of Sandwich Membrane in Cu $(NO_3)_2$ (0.1 M)	
		For TMTMS	For TETDS	For TMTMS	For TETDS
1	0	0.017	0.000	0.014	0.000
2	5	0.022	0.002	0.015	0.006
3	10	0.025	0.005	0.016	0.009
4	15	0.026	0.008	0.017	0.011
5	20	0.027	0.011	0.018	0.014
6	25	0.028	0.014	0.019	**0.018**
7	30	0.028	**0.017**	**0.020**	0.018
8	35	0.028	0.017	0.020	0.018

Table. 4 Experimental values of EMF for TMTMS and TETDS of PVC (blank) and sandwich membranes in Al^{3+}(0.1 M) solution.

S. No	Time (min)	EMF of PVC (Blank) Membrane in $Al(NO_3)_3$		EMF of Sandwich Membrane in $Al(NO_3)_3$	
		For TMTMS	For TETDS	For TMTMS	For TETDS
1	0	0.069	0.025	0.036	0.016
2	5	0.057	0.018	0.035	0.017
3	10	0.050	0.011	0.031	0.018
4	15	0.046	0.009	0.025	0.019
5	20	0.035	0.005	0.023	**0.020**
6	25	0.032	0.001	**0.021**	0.020
7	30	**0.029**	**0.000**	0.021	0.020
8	35	0.029	0.000	0.021	0.020

Table. 5 Experimental results of stability constant (log $\beta_{\mathrm{IL}n}$) for TMTMS as an ionophore with different metal ions.

Metal ion	Stability constant log $\beta_{\mathrm{IL}n}$
Fe^{3+}	4.691
Ni^{2+}	3.720
Cu^{2+}	**6.790**
Zn^{2+}	5.919
Ag^{+}	5.212
Hg^{+}	5.059
Pb^{2+}	5.045
Ca^{2+}	6.393
Na^{+}	5.380
Al^{3+}	5.8587

Table. 6 Experimental results of stability constant (log $\beta_{\mathrm{IL}n}$) for TMTDS as a ionophores with different metal ions.

Metal ion	stability constant log $\beta_{\mathrm{IL}n}$
Fe^{3+}	6.1014
Ni^{2+}	5.350
Cu^{2+}	5.380
Zn^{2+}	6.229
Ag^{+}	5.556
Hg^{+}	5.387
Pb^{2+}	5.045
Ca^{2+}	5.789
Na^{+}	4.981
Al^{3+}	**6.659**

5. CONCLUSION

We have used TMTMS and TETDS thiuram as ion carrier (ionophores) for construction of a sandwich PVC-based membrane sensor to determine stability constants for several metals. It was found that these ionophores show best responses with NPOE plasticizer and NaTPB anionic additive in PVC matrix. The considerably high values of stability constant for copper and aluminium calculated by sandwich PVC membranes confirm that they bind strongly with these ionophores. Further, in future the proposed sensor can also be used for the determination of copper and aluminium ions in several real samples analysis.

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