Determination of silver and mercury ions stability constant with Thiuram ligands using sandwich membrane method

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ABSTRACT

The tetramethylthiuram monosulphide (TMTMS) and tetraethylthiuram disulphide (TETDS) explored as suitable ionophores to investigate the interaction of thiuram ligands with heavy metal ions. Ion selective sandwich membrane method was used to determine stability constants. It displays good $log\beta_{ILn}$ (for Ag+ with TMTMS and TETDS ~6.7 and for Hg+ with TMTMS and TETDS ~6). The response time and life times are 14 s and eight weeks respectively over a wide pH range (3.5 - 9.5). Interference from other metal ions is very low and it can be used as indicator electrode in the potentiometric titration of silver and mercury ions and to determine their concentrations in agricultural soil water samples.

Keywords: Sandwich Membrane Method, Ionophore, Heavy Metal Ions Detections

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INTRODUCTION

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 studied and different techniques have been investigated to determine the stability constant [1-3]. 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 [2-4]. 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 [5,6]. An analogous potentiometric method to determine effective complex formation constants in the organic membrane phase was reported as well [7]. The two methods do have some drawbacks. First, the 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 [8]. 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.

Carrier-based ion-selective electrodes (ISEs) is quite simple, low cost and very effective for the direct selective detection of ionic species in complex samples [9-12]. 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

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blotting [13-15]. 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.

Thiuram sulfides can be used to extract metal ions selectively. Thiuram 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 [16]. In this study tetramethylthiuram monosulphide (TMTMS) and tetraethylthiuram disulphide (TETDS) Fig. 1 are used as ionophores. Kamata *et al.,* proposed that the fungicidal effect of thiuram was connected with their ability to form complexes with the heavy metal ions [17,18]. It thus seemed interesting to investigate the stability constants values of thiuram compounds with metal ions in order to study the mode of its coordination with metal ions [19-20].
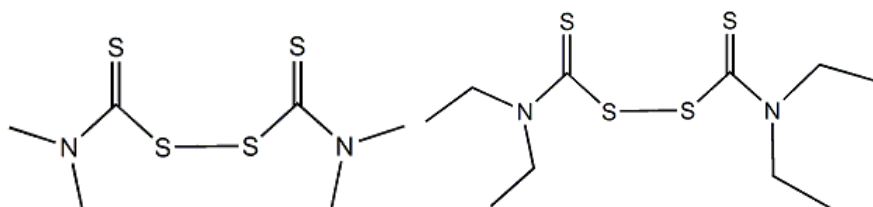

Fig. 1 Structure of tetramethylthiuram monosulphide (TMTMS) and tetraethylthiuram disulphide (TETDS) ionophore

EXPERIMENTAL SECTION

2.1 Reagents
Sodium tetraphenyl borate (NaTPB), o-nitrophenyloctylether (NPOE) was obtained from sigma Aldrich, high molecular weight PVC and tetrahydrofuran (THF). Ionophores TMTMS (tetramethylthiuram monosulphide) and TMTDS (tetraethylthiuram disulphide) were purchased from Sigma-Aldrich. Metal salts $Al(NO_3)_3$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Fe(NO_3)_2$, $Ca(NO_3)_2$, $Hg_2(NO_3)_2$, $Zn(NO_3)_2$ and $Pb(NO_3)_2$ were purchased from Sdfine, NaCl from Loba chem and $AgNO_3$ were purchased from Qualizen. Aqueous solutions (0.1 M) were prepared by dissolving the appropriate salts in distilled water.

2.2 Preparation of Membranes
2.2.1 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 [21-25].

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 [26, 27].

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2.2.2 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 [28]. 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.

2.3 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^{2+} 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.

2.4 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 [29]:

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

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.

2.5 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 [28]. A series of solutions are prepared which contain equal formal

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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.

RESULTS AND DISCUSSION

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.

In order to know the stochiometry of ligands with metal ion, in preliminary experiments TMTMS and 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. 2 and 3.

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 metal ion solution (0.1 M) are represented in Tables 2 and 3.

Table. 1 Optimized composition of various components for membrane preparation

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

Among different tested cations, Ag^+ ion gives best stability constant (6.79) with TMTMS and Hg^+ with TETDS. The stability constant obtained for all other tested cation were lower than these for silver and mercury ions. The determined formation constants ($\log \beta_{ILn}$) for the examined cations were recorded in Table 4.

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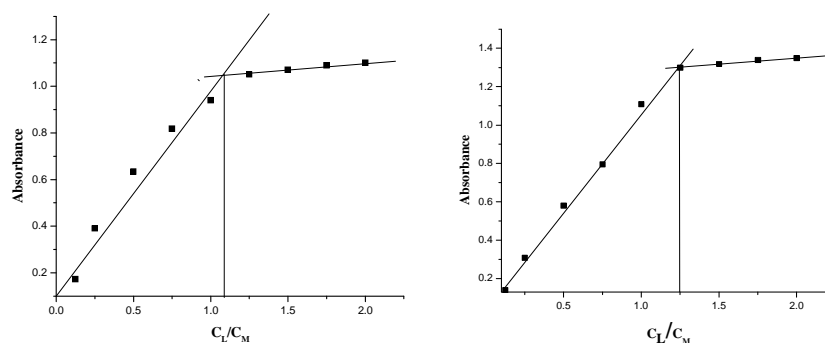
Fig. 2 Determination of stochiometry (~1:1) between TMTMS and TETMS with Ag$^+$ ions
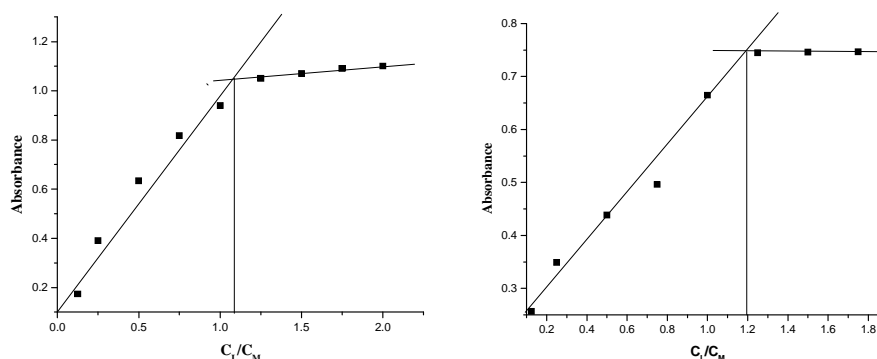
Fig. 3 Determination of stochiometry (~1:1) between TMTMS and TETMS with Hg$^+$ ion

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 Hg$^+$ (0.1 M) solution

S.No	Time(min)	EMF of PVC(Blank) Membrane in Hg$_2$(NO$_3$)$_2$ (0.1 M)		EMF of Sandwich Membrane in Hg$_2$(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

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Table. 4 Experimental results of stability constant (logβ_{ILn}) for TMTMS and TETDS as ionophore with different metal ions

Metal ions	Stability constant log β_{ILn}	
	For TMTMS	For TETDS
Fe^{3+}	4.691	6.1014
Ni^{2+}	3.720	5.350
Cu^{2+}	5.059	5.380
Zn^{2+}	5.212	5.387
Ag^+	**6.790**	**6.659**
Hg^+	**5.919**	**6.229**
Pb^{2+}	5.045	5.045
Ca^{2+}	4.993	5.789
Na^+	5.380	4.981
Al^{3+}	5.858	5.556

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 silver and mercury ions were calculated by sandwich PVC membranes that confirm strong binding with these ionophores. Further, in future the proposed sensors can also be used for the determination of silver and mercury ions in several real samples analysis, especially in agricultural soil water samples.

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