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Polymeric Membrane Sensor for Potentiometric Determination of Tin(II) Ions

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ABSTRACT

Tin(II)-ion-selective electrode consisting of dibenzo-18-crown-6 (DB18C6) as an ionophore in PVC matrix was developed. The influences of membrane composition, selectivity, response time, reversibility and temperature on the electrode performance were investigated. The electrode showed a near Nernstian response for Sn^{2+} ions over a concentration range from $1.0 \times 10^{-6} - 1.0 \times 10^{-2}$ M with a slope of 27.5 ± 0.6 mV per concentration decade in a acidic solution (pH=1). The limit of detection was 8.0×10^{-7} M. It has a relatively fast response time and can be used for at least 3 months without any divergence in potentials. The isothermal temperature coefficient of this electrode amounted to 0.0012 V/ °C. The stability constant (log K_s) of the Sn(II) – DB18C6 complex was determined at 25 °C by potentiometric titration in mixed aqueous solution.

Keywords: ion selective electrode, Poly(vinyl chloride) membrane, potentiometry, Crown ether

INTRODUCTION

The development of selective membrane electrodes based on neutral carriers is one of the most promising trends in ionometry [1]. In the area of membrane based ISEs, emphasis has been focused on the development of new ionophores and on the composition of the membrane phase, aiming at enhancing the potentiometric responses of the ISEs. Fabrication of a new, ion-specific ISE with high selectivity and sensitivity, wide linear concentration range, long lifetime, good reproducibility and low cost, is always in need. Crown ethers have been widely used as suitable neutral carriers for the selective and efficient transport of alkali and alkaline earth cations through liquid membranes and for constructing membrane-selective electrodes for these cations [2,3], mainly due to their specific selectivity and extraction efficiency for metal ions. Generally, a crown ether forms a complex with a metal ion that fits well in its cavity. Solvent polymeric membrane based ISEs together with the incorporation of new ion carriers have shown to be a very useful tool for chemical, clinical, and environmental analysis as for process monitoring [4-7].

A number of methods are today available to measure ion- ionophore formation constant. In some cases, a good correlation between selectivity coefficients and the ratio of experimental formation constants obtained in ordinary polar solvents has been observed [8], However, most ion carriers form very weak complexes in such solvents [9], and most ionophores cannot be characterized with this approach. Therefore, a direct measurement of complex formation constants within the solvent polymeric membrane phase has been shown to yield more meaningful results [10,11].

The results present in this article shows that the sensor developed for Sn (II) ion using DB18C6 as a neutral carrier has a wide working concentration

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range, fast response time and gives reproducible results.

EXPERIMENTAL

1. Reagents and materials

Reagent grade acetophenone (AP), oleic acid (OA), tetrahydrofuran (THF) and high relative molecular weight PVC (all from Merck) were used as received. Chloride and nitrate salts of all other cations and detergent used (all from Merck) were of the highest purity available and used without any further purification. Double distilled deionized water was used throughout.

2. Electrode preparation and potential measurements

The general procedure used to prepare the PVC membrane was to mix thoroughly 30 mg of powdered PVC, 5 mg of ionophore DB18C6, 60 mg of plasticizer AP and 5 mg of additive oleic acid until the PVC was wet. Then the mixture was dissolved in 3 ml of dry freshly distilled THF. The resulting clear mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (5 mm o.d.) was dipped into the mixture for about 10 s so that a nontransparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 1 h. The tube was then filled with internal solution 1.0×10^{-3} M Sn(II) chloride in pH=1. The electrode was finally conditioned for 6 h by soaking in a 1.0×10^{-2} M $SnCl_2$ solution whit pH=1. The ratio of various ingredients [12], concentration of equilibrating solutions and time contact were optimized to provide membranes which result in reproducible, noiseless and stable potentials.

The potential measurements were carried out with the following assembly :

SCE /internal solution, 1.0×10^{-3} M $SnCl_2$ +1.0×10^{-1} M HCl / PVC membrane / test solution / $Hg\text{-}Hg_2Cl_2$, KCl (saturated).

The potentiometric measurements were performed with a Metrohm pH meter E516 at 25.0 ± 0.1 °C. The external reference electrode was a standard calomel electrode (SCE) shielded by an intermediate salt bridge compartment containing the background electrolyte in order to prevent any transfer of potassium ions into the measuring solution. In all cases, a 1.0×10^{-1} mol dm^{-3} HCl solution was used as electrolyte medium.

RESULTS AND DISCUSSION

1. Effect of membrane composition on the electrode response

It is well known that the sensitivity and selectivity obtained for a given ionophore depends significantly on the membrane composition and the nature of solvent mediator and additive used [13]. Thus, the influences of the membrane composition, nature and amount of plasticizer and amount of oleic acid as a lipophilic additive on the potential response of the Sn(II) sensor were investigated and the results are summarized in Table 1. It is seen that, the use of 60 % AP in the presence of 30 % PVC, 5 % ionophore and 5 % oleic acid (No. 3, Table 1) results good electrode performance.

Table 1. Optimization of the membrane ingredients.

No	**Composition(%)**				**Slope (mV/decade)**	**Linear range [M]**
	Ionophore	**PVC**	**Plasticizer**	**Additive**		
1	-	35	60(AP)	5(OA)	1.3	-
2	3	30	62(AP)	5(OA)	17.9	1.0×10^{-6}-1.0×10^{-2}
3	5	30	60(AP)	5(OA)	27.5	1.0×10^{-6}-1.0×10^{-2}
4	8	30	57(AP)	5(OA)	25.8	1.0×10^{-6}-1.0×10^{-2}
5	5	30	62(AP)	3(OA)	19.3	1.0×10^{-5}-1.0×10^{-2}
6	5	30	57(AP)	8(OA)	19.9	1.0×10^{-5}-1.0×10^{-2}
7	5	30	60(DBP)	5(OA)	27.1	4.0×10^{-6}-1.0×10^{-2}
8	8	30	57(DBP)	5(OA)	24.9	1.0×10^{-6}-1.0×10^{-2}
9	5	30	60(AP)	5(KT_pClPB)	24.3	1.0×10^{-5}-1.0×10^{-2}
10	10	30	55(AP)	5(OA)	30.4	1.0×10^{-6}-1.0×10^{-2}

The potential response of the membrane at varying concentration of Sn(II) ion, indicates a rectilinear range from 1.0 × 10^{-6} to 1.0 × 10^{-2} M (Fig. 1). The slope of the calibration curve was 27.5 ± 0.6 mV/decade of Sn(II) concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 8.0 ×10^{-7} M. The standard deviation of 7 replicate measurements is ± 0.6 mV. The membrane sensors prepared could be used for more than 3 months without any measurable change in potential.

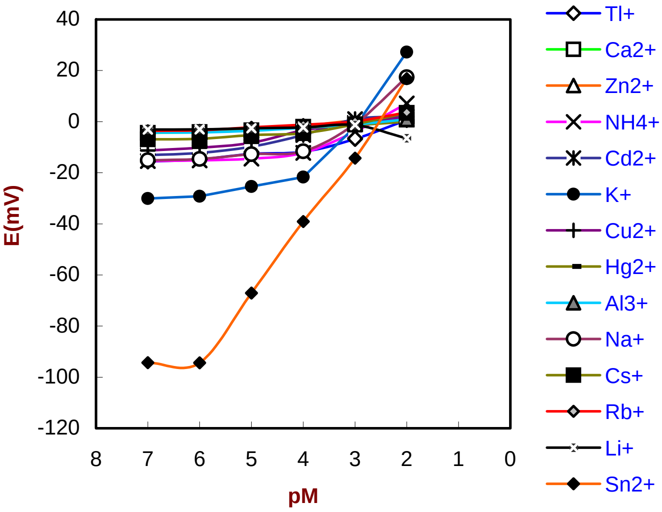

Fig. 1. Potentiometric response of the various ion selective electrode based on DB18C6.

It should be noted that the presence of lipophilic and immobilized ionic additives [14], or salt of two lipophilic ions [15], could diminish membrane resistance, eliminate the diffusion potential [16], and in some cases, change the selectivity pattern of the ion-selective PVC membrane, resulting in a good working performance.

2. potentiometric selectivity

The selectivity coefficients (K_{Sn}^{pot}) of the electrode towards different catonic species (M^{n+}) were determined graphically using the mixed solution method [17], according to the following equation:

$$K_{Sn}^{pot}\, a_M^{2/n} = a_{Sn}\{\exp[(E_2 - E_1) F/RT]\} - á_{Sn} \quad (1)$$

Where E_1 and E_2 are the electrode potentials for the solution of Sn(II) ions alone and for the solution containing interfering ion(M) and Sn(II) ions, respectively. According to Eq. (1), the K_{Sn}^{pot} values for diverse ions can be evaluated from the slope of the graph of $\{ a_{Sn} \{\exp[(E_2 - E_1) F/RT]\} - á_{Sn} \}$ versus $a_M^{2/n}$.

The K_{Sn}^{pot} values were evaluated graphically by the mixed solution method from potential measurements on solution containing a fixed concentration of Sn^{+2} ion (1.0 × 10^{-3} M) and varying amounts of the interfering ions (M^{+n}) (Table 2). As seen from Table 2, whit the exception of Fe^{2+} and Hg^{2+} ions, the selectivity coefficients obtained for all other cations were in the order of 10^{-2} or smaller, indicating that they do not disturb the functioning of the Sn^{2+} ion selective electrode significantly [18]. However, in view of moderate selectivity of the electrode, above-mentioned ions would cause considerable interference for electrode, even if present in comparative amounts. Therefore, in order to realize the level of interference caused by these ions in the performance of electrode, mixed run studies were carried out [19-23].

Table 2. Selectivity coefficient of various interfering ions. Membrane electrodes With the PVC: AP: DB18C6: oleic acid ratio of 30: 60: 5: 5 were used.

M^{n+}	$K^{pot.}_{Sn,M}$	M^{n+}	$K^{pot.}_{Sn,M}$
Al^{3+}	1.2 × 10^{-3}	Cd^{2+}	7.2 × 10^{-3}
Mn^{2+}	3.1 × 10^{-2}	Ca^{2+}	6.3 × 10^{-2}
Mg^{2+}	4.8 × 10^{-2}	Pb^{2+}	4.1 × 10^{-2}
Zn^{2+}	4.5 × 10^{-2}	Hg^{2+}	8.5 × 10^{-2}
Cu^{2+}	3.1 × 10^{-2}	Sr^{2+}	3.8 × 10^{-2}
Co^{2+}	4.4 × 10^{-2}	Bi^{3+}	5.0 × 10^{-2}
Fe^{2+}	1.1 × 10^{-1}	Fe^{3+}	1.7 × 10^{-2}

Fig. 2 shows the variation of potentials with Sn^{2+} ion concentration in presence of different concentration of Fe^{2+}. It is observed that the increasing of the concentration of Fe^{2+} ion would cause decreasing of the detection limit and linear range. Mixed run studies were also carried out for a noninterference ion such as Cd^{2+} ion and result was shown in Fig. 3. It is shown that the presence of Cd^{2+} ions don't overly contribute on membrane potentials.

3. Response time

Dynamic response time is an important factor for an ion-selective electrode [24]. In this study, the practical response time was recorded by changing solution with different Sn^{2+} concentration from 1.0 × 10^{-5} to 7.5 × 10^{-4} M. The actual potential versus time traces is shown in Fig. 4. As can be seen, the electrode reaches the equilibrium response in a short time of about 10 s.

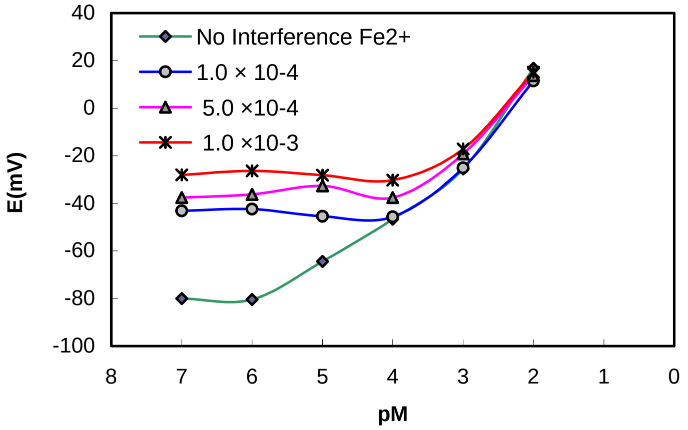

Fig. 2. Effect of different concentrations of Fe^{2+} ions on the variation of potential.

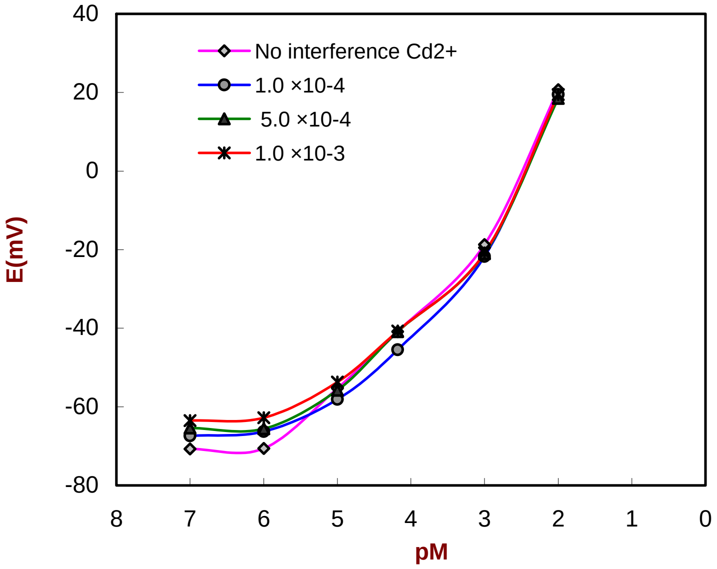

Fig. 3. Effect of different concentrations of Cd^{2+} ions on the variation of potential.

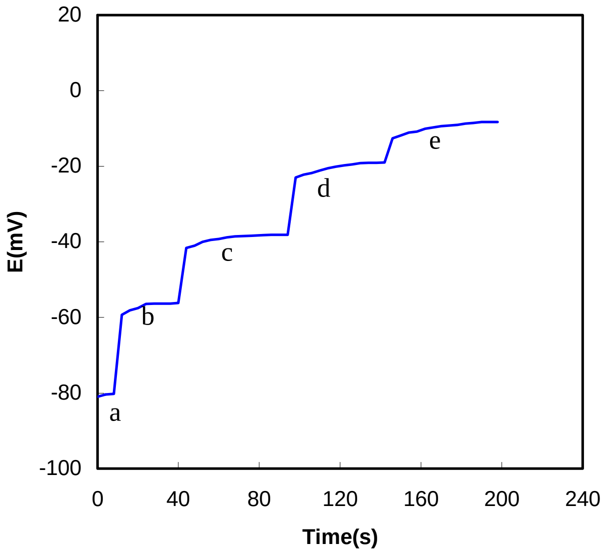

Fig. 4. Dynamic response time of the electrode for step change in concentration of Sn^{2+}; **a)** 1.0×10^{-5} M, **b)** 5.0×10^{-5} M, **c)** 1.0×10^{-4} M, **d)** 5.0×10^{-4} M, **e)** 7.5×10^{-4} M.

Table 3. Performance characteristics of Sn^{2+} - electrode at different temperatures

Temperature(° C)	**Slope (mV/decade)**	**E°_{cell} (mV)**	**Linear range [M]**
25	26.0	75.0	2.5×10^{-6}-1.0×10^{-2}
30	26.5	78.9	2.5×10^{-6}-1.0×10^{-2}
35	27.4	81.2	2.5×10^{-6}-1.0×10^{-2}
40	28.2	84.0	2.5×10^{-6}-1.0×10^{-2}
45	29.4	85.5	2.5×10^{-6}-1.0×10^{-2}

4. Effect of temperature

The trend of changes of electrode performance with temperature, at test solution temperatures 25, 30, 35, 40 and 50 ° C are represented in Table 3. It is clear that the electrode gave a good Nernstian response in the temperature range 20-45. At 50 ° C, the slope of electrode did not show a good Nernstian behavior. This behavior may be due to the following reason: at such high temperatures, the phase boundary equilibrium at the gel layer-test solution interface is disturbed by the thermal agitation of the solution [25].

The standard cell potential, (E°_{cell}) were determined, as the intercepts of the calibration graphs at $pSn^{2+} = 0$, and used to obtain the isothermal temperature coefficient (dE°/dT) of the cell with the aid of the following equation [26]:

$$E^{\circ}_{cell} = E^{\circ}_{cell\,(25\ ^{\circ}C)} + (dE^{\circ}/dT)_{cell}\ (t-25) \qquad (2)$$

A plot of E°_{cell} versus (t- 25) produced a straight line, as shown in Fig. 5. The slope of this line was taken as the isothermal temperature coefficient of the cell. It amounts to 0.00052 V/ °C. The standard potentials of the Hg/Hg_2Cl_2, KCl(sat'd) reference electrode were calculated using the following equation:

$$E^{\circ}_{Hg/Hg2Cl2} = 0.241 - 0.00066\ (t-25) \qquad (3)$$

The values of the standard potentials of Sn(II) – electrode were calculated at the different temperatures from the following relation :

$$E^{\circ}_{cell} + E^{\circ}_{reference} = E^{\circ}_{electrode} \qquad (4)$$

A plot of $E^{\circ}_{electrode}$ versus (t-25) gave a straight line, as shown in Fig. 5. The slope of the line was taken as the isothermal temperature coefficient of the Sn(II) – electrode. It amounts to 0.0012 V/ °C. The small values of $(dE^{\circ}/dT)_{cell}$ and $(dE^{\circ}/dT)_{electrode}$ reveal the high thermal stability of the electrode within the investigated temperature range.

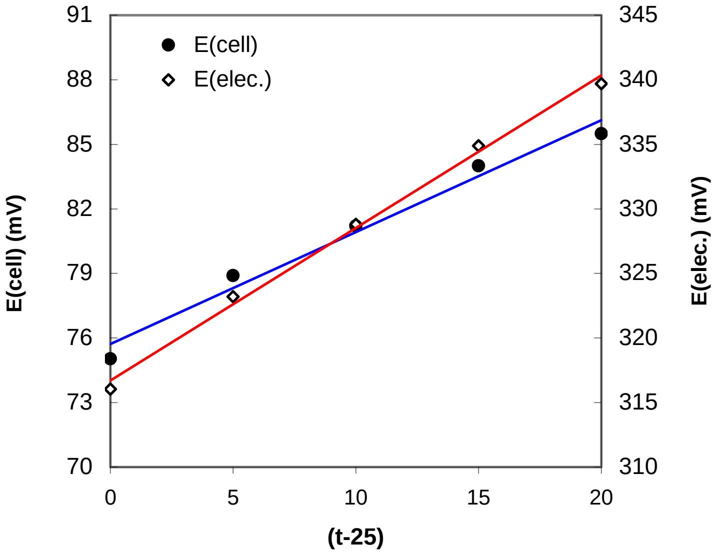

Fig. 5. Variation of standard potential of the cell and electrode whit changes of test solution temperature.

5. *Determination of stability constant*

Potentiometric titrations were performed to measure the complexation behavior of DB18C6 whit Sn^{2+} directly in mixed aqueous solution of water, hydrochloric acid, ethanol and dichloromethane. Using the experimental set-up described in [27], a salt solution (1.0×10^{-3} M) is titrated with a solution containing the ligand (1.0×10^{-2} M). The activity of uncomplexed cation $[Sn^{2+}]$ in solution is calculated from the measured potential E according to the following equation:

$$[Sn^{2+}] = C_M 10^{(E-E_1)/D} \qquad (5)$$

here E_1 is the potential between the Sn(II) - electrode and the reference electrode before titration. The constant D is defined as:

$$D = -\frac{2.303RT}{nF} = -\frac{59.16}{n}(mV) \quad (6)$$

Since the total concentrations of the cation C_M and ligand C_L are known, the concentration of the complex, $[LSn^{2+}]$, can be expressed as:

$$[LSn^{2+}] = C_M - [Sn^{2+}] \qquad (7)$$

The concentration of free ligand [L] is:

$$[L] = C_L - C_M + [Sn^{2+}] \qquad (8)$$

as ligand DB18C6 is added, the concentration of Sn^{2+} is expected to change due to complex formation. The accompanied potential changes from C_L / C_M ratio of 0.2 – 0.8 were measured and used to calculate the stability constant for 1:1 complex as 2685 (i.e. $\log K_s = 3.43 \pm 0.08$) at 25 °C.

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