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Sn (II) Ion- Selective Membrane Electrode based on Dibenzo-18-Crown-6

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ABSTRACT

We found that dibenzo-18-crown-6 (DB18C6) can be used as an ionophore to make a tin (II)-ion-selective membrane electrode. The electrode exhibits a near Nernstian response for Sn^{2+} ions over a concentration range from $1.0\times10^{-6} - 1.0\times10^{-2}$ M with a slope of 27.5 ± 0.6 mV per concentration decade in an acidic solution (pH=1). The limit of detection was 8.0×10^{-7} M. It has a response time of <20s and can be used for at least 3 months without any divergence in potentials. The proposed membrane electrode revealed very good selectivity for Sn^{2+} ions over a wide variety of other cations and could be used in acidic media. It was used as indicator electrode in potentiometric determination of tin (II) ion in real sample.

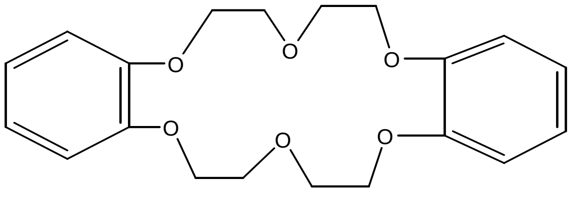
Keywords: Potentiometry, Ion - selective membrane electrode; Tin; Crown ether.

INTRODUCTION

Crown ethers have been demonstrated as highly selective complexing agents for many metal ions. They can be applied in separation and determination of metal ions through molecular recognition. Generally, a crown ether forms a complex with a metal ion that fits well in its cavity. Lariat crown ethers (LCEs) are designed to enhance the cation-binding ability of crown ethers through the co-operative ligation of additional donor atom(s) introduced in a sidearm. Thus, LCEs often exhibit different cation-binding properties from the parent crown ethers. The availability of this improved, highly selective material has made the development of specific sensors possible. In the area of membrane based ISE, 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 [1]. These characteristics have inevitably led to sensors for several ionic species, and the list of available electrodes has grown substantially over the past years [2].

The successful development of these electrodes is, in many respects, determined by the availability of a reliable theory explaining the selective behavior of membranes with neutral carriers and allowing one to formulate the principles governing the design of ionophore structures with preassigned properties. Nowadays, published articles on ionophore-based ion-selective electrodes (ISEs) are increasingly developed [3-7]. 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 analyses as for process monitoring [8-10].

The results present in this article shows that the sensor developed for Sn (II) ion using DB18C6 as a neutral carrier (Scheme1) has a wide working concentration range, fast response time and gives reproducible results.



Scheme 1. Structure of DB18C6

EXPERIMENTAL

1. Reagents and materials

Reagent grade acetophenon (AP), oleic acid (OA), tetrahydrofuran (THF) and high relative molecular weight PVC (all from Merck) were used

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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

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 $\times 10^{-3}$ M tin (II) chloride in pH=1. The electrode was finally conditioned for 6 h by soaking in a 1.0×10^{-2} M SnCl2 solution whit pH=1. The ratio of various ingredients [11], concentration of equilibrating solutions and time contact were optimized to provide membranes which result in reproducible, noiseless and stable potentials.

3. EMF measurement

The EMF measurements were carried out with the following assembly:

Hg-Hg_2Cl_2 /internal solution, 1.0×10^{-3} $SnCl_2$ +1.0×10^{-1} mol dm^{-3} HCl / PVC membrane / test solution / Hg-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.

4. Selectivity

The selectivity coefficients K_{Sn}^{pot} of the electrode towards different cationic species (M^{n+}) were determined graphically using by the mixed solution method [12], 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 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 $_M^{\ 2/n}$.

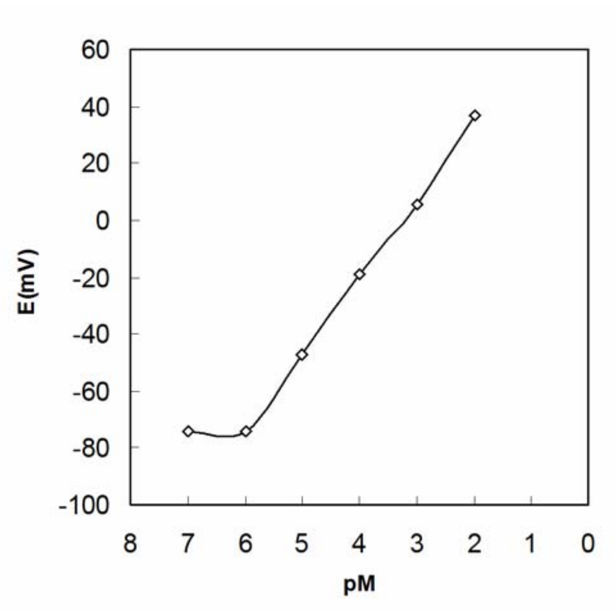

Fig. 1. Calibration plot for the Sn^{2+} sensor.

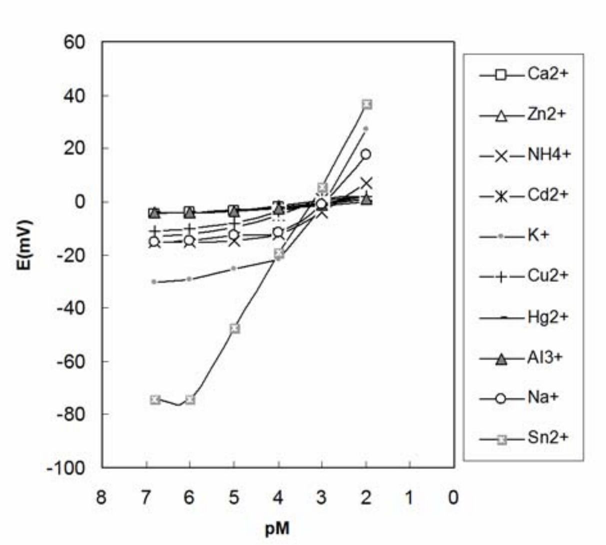

Fig. 2. Potentiometric response of various ion selective electrodes based on DB18C6.

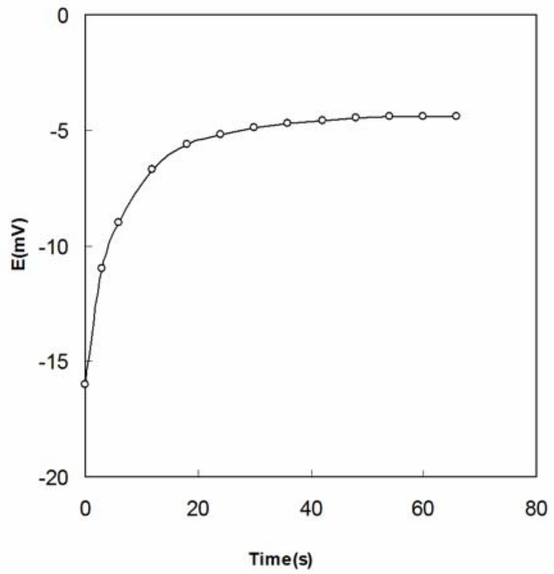

Fig. 3. Response time of the proposed membrane electrode towards Sn^{2+} ions.

RESULTS AND DISCUSSION

1. Effect of membrane composition

It is well known that the sensitivity and selectivity obtained for a given ionophore depend significantly on the membrane composition and the nature of solvent mediator and additives 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 Table1. 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 in the best sensitivity, with a Nernstian slope of 27.5 ± 0.6 mV/decade over a wide relatively dynamic range. It should be noted that the presence of lipophilic and immobilized ionic additives [14, 15] or salt of two lipophilic ions [16] could diminish membrane resistance, eliminate the diffusion potential [17], and in some cases, change the selective pattern of the ion-selective PVC membrane, resulting in a good working performance.

2. Calibration curve and statistical data

The emf response of the membrane at varying concentration of Sn (II) ion (Fig.1) indicates a rectilinear range from 1.0×10^{-6} to 1.0×10^{-2} M. The slopes of the calibration curves were 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.

3. Potentiometric selectivity

Perhaps the most important characteristic of a membrane sensor is its relative response for the primary cation over other cations present in the solution, which is expressed in terms of potentiometric selectivity coefficients (K_{Sn}^{pot}). The K_{Sn}^{pot} values which 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}) (Fig. 2). The resulting values of the selectivity coefficients based on Eq. (1) are summarized in Table 2. As seen from Table 2, whit the exception of Fe^{2+} ion, the selectivity coefficients obtained for all the 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, 19].

4. Response time

The response time, i.e. the time taken by the electrode to achieve stable and low noise potentials. The average time required for the membrane electrode to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of Sn^{2+} ion solutions, each having a 10-fold difference in concentration, was investigated. A potential-time plot for the electrode is given in Fig. 3. The static response time of the PVC membrane thus obtained was 20 s for concentration 1.0×10^{-3} M. It should be noted that the equilibrium potentials essentially remained constant for more than 5 min, after which only a very slow divergence within the resolution of the potentiometer (±1 mV) was recorded.

ANALYTICAL APPLICATION

The percent of Sn in alloy (Sn, Pb) was determined by the proposed sensor. 0.300 g alloy (Sn, Pb) was dissolved in 10 ml of HCl 12 M and then, water was added to bring the volume to about 100 ml. The potential of 10 ml above solution was measured as testing sample (E_u). Then 0.1 ml of 2.5×10^{-2} M, Sn^{2+} standard solution was added into the testing solution and the equilibrium potential of E_s was obtained. From the potential change of ΔE ($E_u - E_s$) one can determine the concentration of the testing sample using the equation given below:

$$C_x = \frac{C_s \times V_s}{(V_x + V_s)10^{\Delta E/S} - V_x}$$

Here C_x is the Sn^{2+} concentration of testing sample, C_s is the concentration of the standard, V_x and V_s are the corresponding volumes, S is the slope of the electrode response, and ΔE is the change in potential [20]. Then Sn% in testing sample was determined (63.3), that it has agreed whit real quantity in alloy (Sn, Pb) 63% (made in Singapore).

ACKNOWLEDGMENT

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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	60(DBP)	5(OA)	27.1	3.0×10^{-6}-1.0×10^{-2}
6	8	30	57(DBP)	5(OA)	24.9	1.0×10^{-6}-1.0×10^{-2}
7	5	30	60(AP)	5(KT_pClPB)	24.3	1.0×10^{-5}-1.0×10^{-2}

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}

REFERENCES

1. *Su, C.C.; Chng, M.C.; Liu, L.K.; Anal. Chim. Acta 432 (2001) 261.*
2. *Bühlmann, P.; Pretsh, E.; Bakker, E.; Chem. Rev, 98 (1998) 1593.*
3. *Mousavi, M.F.; Sahari, S.; Alizadeh, N.; Shamsipur, M.; Anal. Chim. Acta 414 (2000) 189.*
4. *Mousavi, M.F.; Alizadeh, N.; Shamsipur, M.; Zohari, N.; Sens. Actuators B 66 (2000) 98.*
5. *Rahmani, A.; Barzegar, M.; Shamsipur, M.; Sharghi, H.; Mousavi, M.F.; Anal. Lett. 33 (2000) 2611.*
6. *Ammann, D.; Morf, W.E.; Meier, P.C.; Pretsch, E.; Simon, W.; Ion.Sel.Electrode Rev. 5 (1983)3.*
7. *Sing, A.K.; Panwar, A.; Kumar, S.; Baniwal, S.; Analyst 124 (1999) 521.*
8. *Li, Z.Q.; Wu, Z.Y.; Yuan, R.; Ying, M.; Shen, G.L.; Yu, R.Q.; Electrochim. Acta 44 (1999) 2543.*
9. *Ruhollahi, A.; Shamsipur, M.; Anal. Chem. 71 (1999) 1350*
10. *Badr, I.H.A.; Diaz, M.; Hawthorne, M.F.; Bachas, L.G.; Anal. Chem. 71 (1999) 1371.*
11. *Kamata, S.; Bhale, A.; Fukunaga, Y.; Murata, A.; Anal. Chem. 60 (1988) 2464.*
12. *Srinivasan, K.; Rechnitz, G.A.; Anal. Chem. 41(1969) 1203.*
13. *Tavakkoli, N.; Shamsipur, M.; Anal. Lett. 29 (1996) 2269.*
14. *Bakker, E.; Bühlmann, P.; Pretsh, E.; Chem. Rev, 97 (1997) 3083.*
15. *Huser, M.; Gehrig, P.M.; Morf, W.E.; Simon, W.; Lindner, E.; Jeney, J.; Toth, K.; Pungor, E.; Anal. Chim. Acta 63 (1991) 1380.*
16. *Ammann, D.; Pretsch, E.; Simon, W.; Lindner, E.; Bezegh, A.; Pungor, E.; Anal. Chim. Acta 171 (1985) 119.*
17. *Mikhelson, K.N.; Lewenstam, A.; Ddina, S.E.; Electroanalysis 11 (1999) 793.*
18. *Mousavi, M.F.; Arvand, M.; Zanjanchi, M.A.; Electroanalysis 13 (2001) 13.*
19. *Gupta, V.K.; Kumar, P.; Anal. Chim. Acta 389 (1999) 205.*
20. *Buck, R.P.; Lindner, E.; Pure Appl. Chem. 66 (1994) 2527.*