Available online at www.sciencedirect.com

SCIENCE DIRECT®

Sensors and Actuators B 107 (2005) 756–761

SENSORS AND ACTUATORS B CHEMICAL

www.elsevier.com/locate/snb

Tin(II)-selective membrane potentiometric sensor using a crown ether as neutral carrier

H. Aghaie[a,*], M. Giahi[a], M. Monajjemi[a], M. Arvand[b], G.H. Nafissi[c], M. Aghaie[d]

[a] *Department of Chemistry, Science and Research Campus, Islamic Azad University, P.O. Box 14515-775, Tehran, Iran*
[b] *Department of Chemistry, Faculty of Science, Guilan University, P.O. Box 1914, Rasht, Iran*
[c] *Department of Chemistry, Tarbiat Moallem University, P.O. Box 15815-3587, Tehran, Iran*
[d] *Department of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran*

Received 6 August 2004; received in revised form 4 December 2004; accepted 9 December 2004
Available online 21 January 2005

Abstract

A PVC membrane Sn(II)-ion-selective electrode has been constructed using dibenzo-18-crown-6 (DB18C6) as membrane carrier. The sensor shows a near Nernstian response for Sn(II) ions over a concentration range from 1.0×10^{-6} to 1.0×10^{-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 <15 s and can be used for at least 3 months without any divergence in potentials. The proposed membrane electrode revealed very good selectivity for Sn(II) ions over a wide variety of other cations and could be used in acidic media. 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. It was used as indicator electrode in potentiometric determination of Sn(II) ion in real sample.

Keywords: Potentiometric sensor; PVC membrane; Tin(II); Crown ether

1. Introduction

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 formation constant of the ion–ionophore complex within the membrane phase is very important parameter that dictates the practical selectivity of the sensor [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 demonstrated as highly selective complexing agents for many metal ions. They can be applied in separation and determination of metal ions through molecular recognition [2]. Generally, a crown ether forms a complex with a metal ion that fits well in its cavity *t*. 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 [3–5].

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 available [6–10].

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 range, fast response time and gives reproducible results.

---

* Corresponding author. Tel.: +98 21 2586686; fax: +98 21 4817175.
E-mail address: hn_aghaie@yahoo.com (H. Aghaie).

0925-4005/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2004.12.010

2. Experimental

2.1. 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.

2.2. 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 with pH = 1. The electrode was finally conditioned for 6 h by soaking in a 1.0×10^{-2} M $SnCl_2$ solution with pH = 1. The ratio of various ingredients, 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 $SnCl_2 + 1.0 \times 10^{-1}$ M HCl/PVC membrane/test solution/SCE.

The potentiometric measurements were performed with a Metrohm pH meter E516 at $25.0 \pm 0.1\,^{\circ}$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.

3. Results and discussion

3.1. Effect of membrane composition on the electrode response

The potential responses of various ion-selective electrodes based on DB18C6 are shown in Fig. 1. Except for the Sn(II) ion-selective electrode, in all other cases the slope of the corresponding potential–pM plots is much lower than the expected Nernstian slopes. 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 [11]. 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.

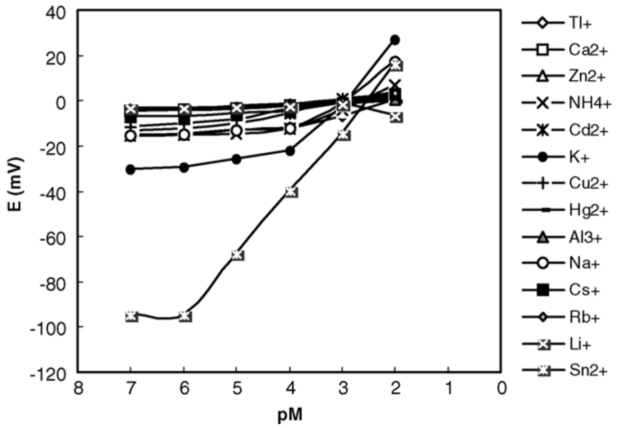

Fig. 1. Response at pH 1 against different cations for ion-selective electrodes containing DB18C6 as ionophore.

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 seven replicate measurements is ±0.6 mV. The membrane sensors prepared could be used for more than 3 months without any measurable change in potential.

It should be noted that the presence of lipophilic and immobilized ionic additives [12,13], or salt of two lipophilic ions [14], could diminish membrane resistance, eliminate the diffusion potential [15], and in some cases, change the selectivity pattern of the ion-selective PVC membrane, resulting in a good working performance.

3.2. Potentiometric selectivity

The selectivity coefficients ($K_{\mathrm{Sn}}^{\mathrm{pot}}$) of the electrode towards different cationic species (M^{n+}) were determined graphically using the mixed solution method [16], according to the following equation:

$$K_{\mathrm{Sn}}^{\mathrm{pot}} a_{\mathrm{M}}^{2/n} = a_{\mathrm{Sn}}\{\exp[(E_2 - E_1)F/RT]\} - \acute{a}_{\mathrm{Sn}} \qquad (1)$$

where E_1 and E_2 are the electrode potentials for the solution of Sn(II)ions alone and for the solution containing interfering