Available online at www.sciencedirect.com
SCIENCE DIRECT
Sensors and Actuators B 114 (2006) 812–818
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

A zinc-selective electrode based on *N*,*N*′-bis(acetylacetone)ethylenediimine

V.K. Gupta [a,*], S. Agarwal [a], A. Jakob [b], H. Lang [b]

[a] *Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, Uttaranchal, India*
[b] *Technische Universität Chemnitz, Fakultät für Naturwissenschaften, Institut für Chemie, Lehrstuhl für Anorganische Chemie, Straße der Nationen 62, 09111 Chemnitz, Germany*

Received 1 March 2005; received in revised form 5 July 2005; accepted 6 July 2005
Available online 22 August 2005

Abstract

The potentiometric response characteristics of electrodes based on *N*,*N*′-bis(acetylacetone)ethylenediimine (**I**) in poly(vinyl chloride) (PVC) combined with an anion localizing agent (sodium tetraphenyl borate, NaTPB) and solvent mediators, viz. *o*-nitrophenyl octyl ether (NPOE), dibutyl (butyl) phosphonate (DBBP), tri-*n*-butyl phosphate (TBP) and chloronaphthalene (CN) were investigated. The best result for Zn^{2+}-sensing was obtained for the electrode membrane of the composition of **I**:PVC:NaTPB:NPOE = 5:100:6:200, where the electrode had a Nernstian response (30.0 mV/decade of Zn^{2+} activity) to Zn^{2+} within the concentration range of 1.0×10^{-6} to 1.0×10^{-1} M. The operational pH range of the electrode was 3.2–7.1. Selectivity characteristic of the proposed electrode was also assessed by calculating $K^{\mathrm{Pot}}_{\mathrm{A,B}}$ with a fixed interference method. The sensor has been successfully used in real sample analysis and also in the potentiometric titration of zinc ions with EDTA.

Keywords: Ion-selective electrodes; Zinc; Schiff base; PVC

1. Introduction

Zinc is relatively rare in nature, but has a long history of use. Its compounds are widely used in, for example, electroplating, pharmaceuticals, paint, rubber, dye, wood preservatives, ointments and battery industries and it is present in wastes and effluents of these units in the form of $ZnCl_2$, $ZnSO_4$, ZnO and ZnS [1]. The estimation of zinc in such wastes is important, because a high dose of zinc (10–15 times more than the RDA, i.e. 10–15 mg/day; RDA is recommended dietary allowance) can cause stomach cramps, vomiting, nausea, severe anemia, pulmonary manifestation and renal failure. Consuming too little zinc is at least as important a health problem as consuming too much zinc. Without enough zinc in the diet, loss of appetite, decreased immune function, slow wound healing and poorly developed male sex organ may occur. Thus, in view of its toxicity and deficiency, the determination of zinc becomes important.

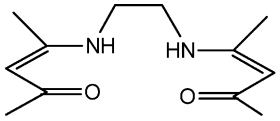
The development and application of ion selective electrodes continue to be an interesting area of analytical research as they provide accurate, rapid, non-destructive and low cost methods of analysis. Besides this, online monitoring is possible by these devices but efforts made so far for developing good zinc-selective electrodes [2–15] have not been very successful. Most of them have poor selectivity [2–4,15], sensitivity and stability, long response time [5,8,10] and short lifetime [6].

A significant number of macrocycles, from crown ethers to calixarene derivatives, have been used in the construction of poly(vinyl chloride) (PVC) membrane electrodes for alkali metal and alkaline earth metal ions [16]. It is well known that the substitution of some oxygen atoms of crown ethers by nitrogen atoms drastically decreases the

* Corresponding author. Tel.: +91 1332 285801/285043; fax: +91 1332 273650.
E-mail addresses: vinodfcy@iitr.ernet.in, vinodfcy@yahoo.com (V.K. Gupta).

0925-4005/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2005.07.039

formation constant of alkali and alkaline earth metal complexes, while the substituted crown ethers show a considerable increase in the stability of their complexes with soft transition and heavy metal ions [17–19]. Considering all the above facts, we synthesized and used successfully *N*,*N*′-bis(acetylacetone)ethylenediimine (**I**) [20], having two nitrogen and two oxygen atoms as ligating sites, as an electroactive material in the PVC matrix for the fabrication of Zn^{2+} selective electrode and the results are presented in this paper.



I

N,N'-Bis(acetylacetone)ethylenediimine

2. Experimental

2.1. Reagents

All reagents used in the investigations were of analytical reagent grade (BDH, UK). Doubly distilled water was used for preparing all aqueous solutions. Sodium tetraphenyl borate (NaTPB) and tri-*n*-butyl phosphate (TBP) from BDH (UK), *o*-nitrophenyl octyl ether (NPOE) from Acros Organics (Belgium), dibutyl (butyl) phosphonate (DBBP) from Mobil (USA) and 1-chloronaphthalene (CN) from Merck (Germany) were used. Molecule **I** was synthesized by a published procedure [20].

2.2. Apparatus

The potential measurements were carried out at $25 \pm 0.1\,^{\circ}C$ with a digital pH meter/millivoltmeter (Toshniwal Inst. Mfg. Pvt. Ltd., Ajmer, India). pH measurements were made on a digital pH meter (LabIndia pH Conmeter, India). Glass electrode as a pH electrode and calomel as a reference electrode were used. Blood samples were dried over IR lamp (Infraphil, Philips) and were analyzed by AAS (Perkin-Elmer, 3100).

2.3. Electrode preparation

The general procedure [21] to prepare PVC based membranes was to dissolve PVC, *N*,*N*′-bis(acetylacetone)ethylenediimine (**I**) and anion localizing agents in ~20 mL THF. After complete dissolution, the mixture was poured in the acrylic rings placed on a smooth glass plate and allowed to evaporate at room temperature. The resulting 0.5 mm thick transparent membrane was cut to size and attached to Pyrex tube. It was finally conditioned for 1 day by soaking in a 0.5 M Zn^{2+} solution. The plasticizers were also added prior to pouring it into the acrylic rings to get membranes of different compositions and those membranes, which generated stable and noiseless potentials, were selected for further studies.

2.4. EMF measurements

The electrode potential (EMF) measurements were performed at 25 °C by using the following electrochemical cell system [22].

External saturated calomel electrode (SCE)	Test solution	Membrane	Internal solution	Internal saturated calomel electrode (SCE)

A 10^{-1} M $Zn(NO_3)_2$ was taken as an inner reference solution and all the standard or test solutions (10^{-7} to 10^{-1} M) were prepared by successive dilution. The performances of electrodes were accessed by measuring the EMFs of the test solutions from low (10^{-7} M) to high (10^{-1} M) concentration, while stirring with a magnetic stirrer.

2.5. Synthesis of *N*,*N*′-bis(acetylacetone)ethylenediimine (*I*)

The synthesis of *N*,*N*′-bis(acetylacetone)ethylenediimine (**I**) was carried out as described by McCarthy et al. [20]. Anhydrous ethylenediamine (60 g; 1.0 mol) was added slowly to 200.24 g (2.0 mol) of acetylacetone. Considerable heat was evolved during the reaction, with the result that the water formed boiled away. The product solidified on cooling to a straw-colored substance. After two times crystallization from water and after being dried under reduced pressure, the colorless solid melted at 111–111.5 °C (yield: 135 g; 0.602 mol, 60% based on ethylenediamine). IR [cm^{-1}, KBr]: 1613 [$\nu_{C=O}$], 1580 [$\nu_{C=N}$]. ^1H NMR (250.13 MHz, in $CDCl_3$) [δ]: 1.83 (s, 6H, CH_3), 1.92 (s, 6H, CH_3), 3.33–3.36 (m, 4H, CH_2), 4.92 (s, 2H, CH), 10.82 (br s, 2H, NH). 13C{^1H}NMR (62.90 MHz, in $CDCl_3$) [δ]: 18.81 (CH_3), 29.01 (CH_3), 43.64 (CH_2), 96.2 (CH), 162.96 (C=N), 195.58 (C=O).

3. Results and discussion

3.1. Response characteristics of the sensor

In preliminary experiments, the potentiometric response of the zinc-selective electrode based on bis(acetylacetone)ethylenediimine (**I**) was examined in a concentration range of 1.0×10^{-7} to 1.0×10^{-1} M. The data summarized in Table 1 indicate that the electrode no. 1, with only **I** and an anion localizing agent (NaTPB) embedded in the PVC matrix, showed the linear response in the concentration range of 8.9×10^{-5} to 1.0×10^{-1} M a with a near-Nernstian slope of 31.5 mV/decade. It is well known that the addition of a lipophilic anion localizing agent not only reduces the ohmic resistance [23] and anionic interference [24], but also improves selectivity [25,26]. Since the nature of a plasticizer influences the dielectric constant of the membrane phase, the