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Potentiometric studies of *N*,*N*′-Bis(2-dimethylaminoethyl)-*N*,*N*′-dimethyl-9,10 anthracenedimethanamine as a chemical sensing material for Zn(II) ions

Nidhi Rani Gupta [a], Susheel Mittal [a,*], Subodh Kumar [b], S.K. Ashok Kumar [a]

[a] *School of Chemistry and Biochemistry, Thapar University, Patiala, 1470 04, India*
[b] *Department of Chemistry, Guru Nanak Dev University, Amritsar, 143005, India*

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Abstract

A liquid membrane based Zn^{2+} ion selective electrode containing *N*,*N*′-Bis(2-dimethylaminoethyl)-*N*,*N*′-dimethyl-9,10 anthracenedimethanamine (Bis(TMEDA) anthracene) (I) as ionophore has been prepared and characterized. The membrane comprises of PVC, ionophore and plasticizer in the ratio of 33:2:65, respectively. It showed the best response in terms of detection limit (1.5×10^{-6} M) and working concentration range (1.0×10^{-5} M to 1.0×10^{-1} M) with Nernstian response towards Zn^{2+} ions. The electrode responds within 15 s of coming in contact with the solution. The potential response remains almost unchanged over a pH range of 3.0 to 7.5. The electrode can be used for at least 3 months without any considerable alteration in its response behavior. The proposed electrode revealed good selectivity towards Zn^{2+} ions over a number of alkali, alkaline earth, transition metals and some other heavy metal ions. The electrode has been used as an indicator electrode in the potentiometric titration of Zn^{2+} with EDTA. The proposed electrode also detected Zn^{2+} ions from real life samples.

Keywords: Poly vinyl chloride (PVC); Ionophore; Liquid membrane; Selectivity coefficients; Indicator electrode; Zinc ions

1. Introduction

Ion selective electrode has been the subject of rapidly increasing interest for analytical chemists over the past few decades [1,2]. The growth of ion selective electrodes is partly due to its low cost, good selectivity and convenience in application. Zinc ions are present in the effluent of industries such as electroplating, pharmaceutical, rubber, dye, batteries, etc. These ions are toxic to human being when present in concentration beyond 124 mg/m^3 i.e. its Threshold Limit Value [3]. Zinc is used in a number of alloys such as brass and bronze, and in batteries, fungicides, and pigments. Zinc is an essential growth element for plants and animals but at elevated levels it is toxic to some species of aquatic life. Zinc most commonly enters the domestic water supply from deterioration of galvanized iron and dezincification of brass. In such cases lead and cadmium also may represent because they are impurities of zinc used in galvanizing. Zinc in water may also result from industrial waste pollution. Hence, there is an urgent need for the selective potentiometric determination of minute amounts of zinc ions, especially in food, biological and environmental samples. In this respect many compounds have been employed as an ionophore in the construction of ISEs for zinc ions [4–15].

Most of the ionophores used in earlier reports were based on compounds like amides, imines etc., which do contain nitrogen as a heteroatom [16–18]. Nitrogen ligands coordinate with transition metal ions as exclusive donor atoms. In this respect, macrocyclic and non-cyclic compounds containing nitrogen donors have attracted wide spread attention, owing to their unique properties [19]. In aqueous solution little reaction occurs between nitrogen ligands and either alkali or alkaline earth metal ions but the stability of the complexes with transition metal ions is markedly enhanced [20–22].

The detailed literature survey shows that the reported zinc selective electrodes are suffering from the following properties

* Corresponding author. Fax: +91 175 2364498.
E-mail address: smittal@tiet.ac.in (S. Mittal).

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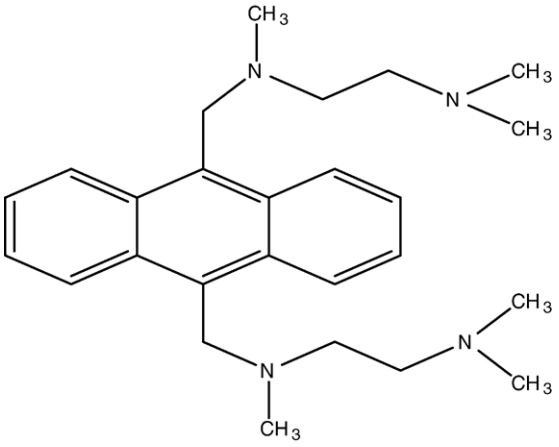

Fig. 1. Structure of (I).

like, poor sensitivity, poor selectivity towards zinc ions in presence of Cu^{2+}, Cd^{2+}, Pb^{2+}, etc., poor stability, long response time and short lifetime [23–27]. These difficulties promoted us to find an ionophore suitable to function as a receptor for zinc selective electrode which is better than the reported ones on many counts and discussed in detail in the text. Therefore, the behavior of (I) with 2 donating nitrogen atoms on both side of TMEDA was investigated as a neutral carrier in the construction of PVC-based membrane for the estimation of zinc ions. Recently, 9,10,Bis-(2-aminophenylthiomethyl)anthracene has been reported as silver selective electrode [28] in which 2 nitrogen and 2 sulphur atoms are involved in bonding with the metal ion. In the proposed work we are reporting (I) as a novel neutral ionophore (Fig. 1) for monitoring of zinc in various samples. Huston et al. in 1986 synthesize this compound and since then it has not been used as an ion sensing material. The fluorescence emission intensity of (I) increases over 1000 fold in the presence of Zn^{2+} indicating the strong affinity for these ions [29,30].

Further, stability constants have been determined for a number of complexes of some metal ions with TMEDA by conductometric method at 25 °C using acetonitrile as a solvent [31]. The calculated log K_f values for Zn^{2+}, Cd^{2+}, Hg^{2+}, $Pb^{2+}$and Ag^{+} are 4.22±0.2, 3.0±0.3, 3.14±0.3, 3.0±0.3 and 3.46±0.2, respectively which show highest stability for zinc ions as compared to other ions. Complexation occurs between zinc ions and nitrogen atoms of the ligand and the resulting complexes are highly stable and selective for zinc ions. These lipophilic ligands, when incorporated into membranes behave as sensing materials for zinc ions.

2. Experimental

2.1. Reagents and apparatus

The ionophore *N*,*N*′-Bis(2-dimethylaminoethyl)-*N*,*N*′-dimethyl-9,10 anthracenedimethanamine (Molecular Formula $C_{26}H_{38}N_4$ Molecular Weight = 406.61) was purchased from Fluka (Buchs, Switzerland, puriss grade). Plasticizers viz., Dibutyl phthalate (DBP), Dioctyl phthalate (DOP), Bis-2-ethyl sebacate (BES), and *ortho*-Nitrophenyloctylether (*o*-NPOE) and all the metal salts were obtained from Aldrich Chemical Company, USA. All solvents used in the investigations were of analytical reagent grade. Aqueous salt solutions were prepared by dissolving the appropriate salt in double distilled water. Potentials were measured with digital potentiometer EQ-602 Equiptronics (accuracy, 0.001 V, India). pH measurements were carried out on an ISFET pH meter (Delta Track, USA).

2.2. Membrane and electrode preparation

All liquid membranes were prepared by the standard procedure given by J.D.R. Thomas et al. [32]. Different membranes were prepared by dissolving 200 mg of a mixture of an ionophore, plasticizer and PVC (as given in Table 1) in 2–3 mL of THF. The amount of ionophore was varied from 1% to 5%. Different plasticizers viz. *o*-NPOE, DBP, DOP and BES were also added to get membranes of different characteristics. The membrane cocktail was then poured in a glass ring of 30 mm diameter placed on a Pyrex glass plate and allowed to evaporate at room temperature for about 24 h. The membrane was then removed from the glass ring and circular pieces of 1.25 cm diameter were cut and mounted on Pyrex glass tubes with suitable adhesive and conditioned with Zn^{2+} solution (0.1 M) for 24 h. The ratio of ionophore and different additives in the membrane was optimized so that it should give good response in terms on Nernstian slope, working range, detection limit, etc. The membrane should also give reproducible and noiseless potentials.

Table 1
Response characteristics of PVC-based membranes with the variations in amounts of the ionophore and nature of the plasticizer

Electrode no.	Components of the membrane (% w/w)			Slope, (mV/decade)	Working concentration range (M)	Detection limit, (M)
	(I)	PVC	Plasticizer			
1.	1	33	66 (NPOE)	24.0±0.8	5.0×10^{-5}–1.0×10^{-1}	1.2×10^{-5}
2.	2	33	65 (NPOE)	30.0±0.5	1.0×10^{-5}–1.0×10^{-1}	1.5×10^{-6}
3.	3	33	64 (NPOE)	34.0±0.7	7.9×10^{-5}–1.0×10^{-1}	1.0×10^{-4}
4.	4	33	63 (NPOE)	36.0±0.8	5.0×10^{-4}–1.0×10^{-1}	6.3×10^{-4}
5.	5	33	62 (NPOE)	40.0±0.8	5.0×10^{-4}–1.0×10^{-1}	1.0×10^{-4}
6.	2	33	65 (DBP)	35.0±0.6	2.5×10^{-5}–1.0×10^{-1}	1.5×10^{-5}
7.	2	33	65 (DOP)	20.0±0.7	3.9×10^{-3}–1.0×10^{-1}	3.1×10^{-4}
8.	2	33	65 (BES)	25.0±0.8	7.9×10^{-3}–1.0×10^{-1}	5.0×10^{-4}