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Ni(II) selective sensors based on Schiff bases membranes in poly(vinyl chloride)

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ABSTRACT

The two nickel chelates of Schiff bases, 3-hydroxy-*N*-{2-[(3-hydroxy-*N*-phenylbutyrimidoyl)-amino]-phenyl}-*N*′-phenylbutyramidine (M_1) and bis-4-(ethyliminomethyl)naphthalene-1-ol (M_2), have been synthesized and explored as ionophores for preparing PVC-based membrane sensors selective to nickel ion. The influences of membrane compositions on the potentiometric response of the electrodes have been found to substantially improve the performance characteristics. The best performance was obtained with the electrode having a membrane composition (w/w; mg) of (M_1): PVC:NaTPB:CN in the ratio 5:150:5:150. The sensor shows a linear potential response for Ni^{2+} over a wide concentration range 1.6×10^{-7} to 1.0×10^{-2} M with Nernstian compliance (30.0 ± 0.2 mV/decade of activity) within pH range 2.5–9.5 and a fast response time of 10 s. The sensor has been found to work satisfactorily in partially non-aqueous media up to 20% (v/v) content of methanol, ethanol, and acetonitrile and could be used for a period of 4 months. The analytical usefulness of the proposed electrode has been evaluated by its application in the determination of nickel in real samples. The practical utility of the membrane electrode has also been observed in the presence of surfactants.

1. Introduction

Nickel is used for many industrial applications therefore present in environment. It is toxic metal and known to cause pneumonitis, asthma, and cancer of lungs and also cause disorder of respiratory and central nervous system [1]. A number of methods, Such as atomic absorption spectrometry (AAS), flame atomic absorption spectrometry-electro thermal atomization (AAS-ETA) [2–5], ICP-AES and flame photometry [6] can be used for determination of nickel. However these methods generally require sample pretreatment and infrastructure backup and are therefore, not very convenient For routine analysis of large number of environmental samples. So there is critical need for the development of selective, portable, inexpensive diagnostic tool for the determination of nickel.

Analytical methods based on potentiometric detection with ion-selective electrodes (ISEs), can be considered as an advantageous alternative because they are ecofriendly, convenient, fast, easy to operate, generally require no sample pre-treatment. Therefore a number of nickel sensors based on heterogeneous membranes of porphyrins [7,8], crown ethers [9–11], cyclams [12–14], ion exchangers [15,16], pentacyclooctaaza [17], 2,5-thiophenylbis (5-tertbutyl-1,3-benzexazole) [18], and Schiff base [19] in PVC. Nickel phosphate [20] in paraffin and silicone rubber, and nickel complex of 1,4,8,11-tetraazacyclotetradecane [21] in araldite has been reported. However, their performance is poor with regard to one or more electrode characteristics, i.e., working concentration range, selectivity, response time, pH range and lifetime. Besides, these solid membrane sensors, liquid membrane sensors for

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nickel using O,O-diisobutyldithiophosphatonickel(II) complex [22] in chlorobenzene, tetradecyl phosphonium–Ni(II) ion pair [23] in chloroform and dichloroethane, bis(tetraethyl ammonium) bis(dithiobenzophenazine)nickelate [24] in nitrobenzene and nickel diethyldithiocarbamate [25] in chloroform and Schiff bases [26,27] in nitrobenzene have also been investigated. However, they are of limited use in view of attrition of liquid membrane during experimentation. It is, thus, necessary to have a better Ni^{2+} sensor and efforts are still being made toward this aim. Thus, newer materials synthesized are continuously being examined for such role. Continuing efforts in this direction, we recently synthesized two Schiff bases and their membranes in PVC matrix as Ni^{2+} selective sensors. The results of this investigation are presented in this paper.

2. Experimental

2.1. Reagents

High molecular weight poly (vinyl chloride) (PVC) Aldrich (Wisconsin, USA), dioctylphthalate (DOP), Renkem (Gurgaon, India), tri-*n*-butylphosphate (TBP), BDH (Poole, England), chloronaphthalene (CN), dibutylphthalate (DBP) and dibutyl (butyl) phosphate (DBBP), Mobile (Alabama, USA), sodium tetraphenyl borate (NaTPB), BDH (Poole, UK) were used as obtained. Analytical reagent-grade tetrhydrofuran (THF), nitric acid, sodium hydroxide were obtained from Ranbaxy (Gurgaon, India). 1,4-Butadiamine and 4-hydroxynaphthaldehyde were from Avon Organics Limited (Greenland, Hydrabad, India). Solution of metal salt (nitrates) was prepared in double-distilled water. Working solution of different concentrations was prepared by diluting 0.1 M stock solutions.

2.2. Synthesis of ionophore

2.2.1. Synthesis of 3-hydroxy-N-{2-[(3-hydroxy-N-phenylbutyrimidoyl)-amino]phenyl}-N′-phenylbutyramidine (M_1)

The ionophore was synthesized as previously described [28]. An ethanolic solution (40 mL) of *o*-phenylenediamine (0.545 g, 0.005 M) was refluxed with acetoacetanilide (1.77 g, 0.01 M) for 12 h. The volume of the solution was reduced to one third and 10 mL of petroleum ether (60–80 °C range) was added with constant stirring. The pale yellow solid acetoacetanilido-*o*-phenylenediamine (M_1) formed was filtered and recrystallised from ethanol. Yield: 60% (mp 83 °C). ^1H NMR (DMSO) δ: 6.9–7.8 (m, Ar–H), 2.49 (–PhNH), 6.3 (=C–CH), 11.8 (–OH). IR, (KBr, cm^{-1}), 1650, 1310, 3150. Elemental analysis % observed for $C_{23}N_4H_{24}O_2$, C = 70.9; N = 14.12; H = 6.12; O = 8.24 and calculated % was C = 71.13; N = 14.43; H = 6.18. The observed elemental analysis of the compound was consistent with the theoretical data obtained on the basis of the structure as given in Fig. 1.

2.2.2. Synthesis of bis-4-(ethyliminomethyl) naphthalene-1-ol (M_2)

The naphthaldehyde-based Schiff base (ionophore) was synthesized by addition of 1,4-diaminobutane (0.01 mol), drop wise to 4-hydroxynaphthaldehyde (0.02 mol) with constant stirring at 60 °C, followed by refluxing for 6 h. The solution was vacuumed to evaporate solution, the residues was dried over $CaCl_2$. Yellow solid, yield 76%, mp 167 °C. ^1H MR (DMSO): δ 6.8–8.08 (m, 10 H, Ar–H), 5.13 (bs, –OH), 8.13 (bs, CH=N), 1.65 (bs, CH_2), 3.55 (bs, CH_2). IR (KBr) 1634, 3452, Elemental analysis % observed for $C_{26}N_2H_{24}O_2$, C = 79.8; N = 6.8; H = 5.9; O = 7.9 and calculated % was C = 78.7; N = 7.0; H = 6.0 and O = 8.0. The observed elemental analysis of the compound was consistent with the theoretical data obtained on the basis of the structure as given in Fig. 1.

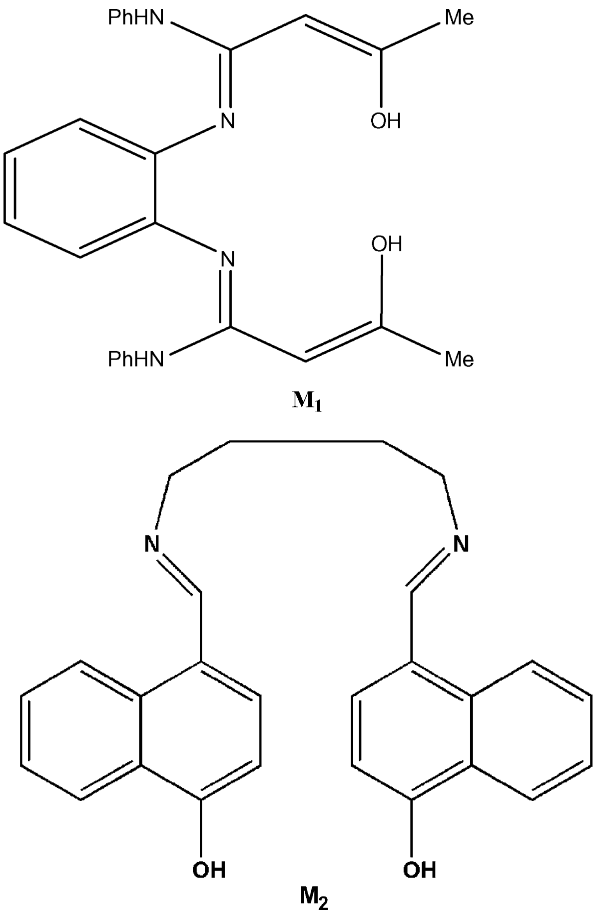

Fig. 1 – Naphthaldehyde-based Schiff base 3-hydroxy-N-{2-[(3-hydroxy-N-phenylbutyrimidoyl)-amino]phenyl}-N′-phenylbutyramidine (M_1) and acetoacetanilide-based Schiff base bis-4-(ethyliminomethyl)naphthalene-1-ol (M_2).

2.3. Fabrication of electrodes

The PVC-based membranes were prepared by dissolving appropriate amounts of Schiff bases (M_1 or M_2), anion excluder NaTPB, solvent mediators, dioctyl phthalate (DOP), tri-*n*-butylphosphate (TBP), 1-chloronaphthalene (CN) and dibutyl(butyl)phosphonate (DBBP) and appropriate amounts of PVC in THF (5 mL). After complete dissolution of all components and thorough mixing, the resulting mixture was poured into polyacrylate rings placed on a smooth glass plate. THF was allowed to evaporate for about 24 h at 25 °C.