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Electrochemical sensors for the determination of Zn^{2+} ions based on pendant armed macrocyclic ligand

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ABSTRACT

The construction and performance characteristics of polymeric membrane electrodes based on two newly synthesized macrocyclic ligands 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene-9,12-N$_2$-1,5-O$_2$ (L_1) and 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,14-diene-9,12-dimethylacrylate-9,12-N$_2$-1,5-O$_2$ (L_2) for the quantification of Zn^{2+} ions are described here. Several membranes having different compositions of PVC, plasticizers, ionic additives and ionophores were fabricated and the best response was observed for the membrane having composition L_2:PVC:TBP:NaTPB in the ratio of 4:37:57:2 (w/w; mg). The response characteristics of the membrane based on L_2 were compared with polymeric membrane electrode (PME) as well as with coated graphite electrode (CGE). The electrode exhibits Nernstian slope for Zn^{2+} ions with limits of detection of 3.3×10^{-7} mol L^{-1} for PME and 7.9×10^{-8} mol L^{-1} for CGE with response time of 12 s and 10 s for PME and CGE respectively. Furthermore, the electrodes generated constant potentials in the pH range of 3.0–8.0 for PME and 2.5–9.0 for CGE. The practical utility of the CGE has been demonstrated by its usage as an indicator electrode in potentiometric titration of EDTA with Zn^{2+} ion solution. The high selectivity of CGE also permits their use in the determination of Zn^{2+} ions in water, biological, milk and tea samples.

1. Introduction

During the past two decades, an extensive effort has been made in the synthesis and characterization of neutral ionophores possessing high selectivities for specific metal ions to develop new potentiometric and optical sensors for the determination of the respective metal ions in real samples. The design and synthesis of new functionalized macrocyclic ligands for specific analytical applications has been the subject of continuous recent interest [1–3]. The complexation properties of polyaza macrocycles are governed mainly by macrocyclic ring size. N-Functionalization of these macrocycles can enhance their metal ion selectivity and stability of metal complexes depending on the coordination properties of the pendant arms. Thus, they have been widely used as suitable neutral ion carriers for constructing membrane selective electrodes for metal ions.

Zinc ion is an important divalent cation in biological systems, and plays important roles in a human body, influencing DNA synthesis, microtubule polymerization, gene expression, apoptosis, immune system function, and the activity of enzymes such as carbonic anhydrase and matrix metalloproteinase [4]. Moreover, zinc ion is also a contributory factor in neurological disorders such as epilepsy and Alzheimer's diseases [5]. Zinc is also essential to the senses of taste and smell and for growth and development. The zinc deficiency was marked by dwarfism or severe growth retardation, as well as, can result in metabolic changes such as impaired immune response, abnormal taste and abnormal dark adaptation. The foods with high content of protein are abundant source of zinc, such as shellfish, meals, liver and milk which is a good source for infants. Zinc is a relatively non-toxic element; however, it can be toxic if consumed in large quantities. For example, zinc is a metal pollutant of environment, significant concentrations of which may reduce the soil microbial activity causing phytotoxic effect [6,7] and also a common contaminant in agricultural and food wastes [8]. Zinc ions are toxic to human beings when present in concentration beyond 124 mg/m^3, *i.e.* its threshold limit value [9]. A high zinc intake is known to produce copper-deficiency anemia by inducing the intestinal cells to synthesize large amounts of a protein that captures copper in a non-absorbable form [10]. Determination of zinc in excretive organ of the human body such as hair can reflect the cumulative status of this essential element in the body evaluating the nutrient status [11]. Thus, the determination of trace amounts of zinc is currently of great interest in many scientific fields, including medicine analyses and environmental monitoring.

Though a number of analytical techniques such as inductivity coupled plasma atomic emission spectroscopy (ICP-AES) [12], UV–vis spectroscopy [13], potentiometry [14], flame atomic absorption spectrometry [15] and voltammetric methods [16]

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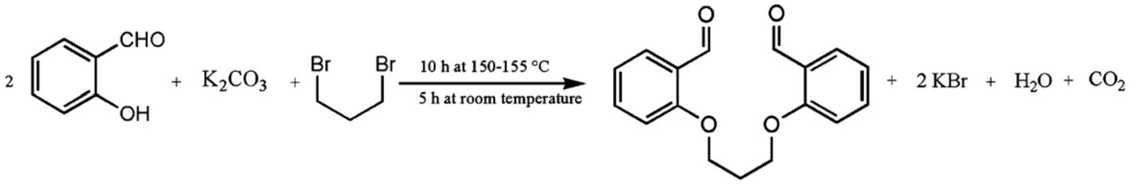

Scheme 1. Synthesis of 1,4-bis(2-carboxyaldehydephenoxy)butane.

have been used to detect trace amounts of zinc, but these methods suffer from a variety of drawbacks, *i.e.* they are costly, and are not appropriate for large-scale monitoring. Potentiometric sensors based on ion-selective electrodes (ISEs) can overcome these limitations and have advantages such as selectivity, sensitivity, high precision, simplicity, wide linear range, low cost, and rapid determination of a variety of ions in different types of sample. The key component of a membrane sensor is the incorporated ionophore, which defines the selectivity of the sensor via. selective complex formation with the cation of interest. A large number of active compounds, for example, crown ethers [17], porphyrins [18], macrocycles [19,20], sulfide drugs [21], cryptands [22], chalcogenides [23], polypyrrole [24], thiazolidin-4-one [25], N,N′-bis(acetylacetone)ethylenediamine [26], bis(2-nitrophenyl) disulfide [27] and tripodal chelating ligand [28] have been explored as ionophores for the construction of ion-selective sensors for Zn^{2+} ions. These reported ISEs have some limitations such as narrow working concentration range, low pH range, substantial interference from a variety of cations, and high response time. There is, therefore, a need to develop a better sensor for zinc ions.

The purpose of the present work is to devise an electrode which is quite selective to Zinc ions and exhibits good response properties using 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene-9,12-N$_2$-1,5-O$_2$ (L_1) and 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,14-diene-9,12-dimethylacrylate-9,12-N$_2$-1,5-O$_2$ (L_2) macrocyclic ligands.

2. Experimental

2.1. Reagents

Reagent grade sodium tetraphenylborate (NaTPB), potassium tetrakis *p*-(chloro phenyl)borate (KTpClPB), dibutylphthalate (DBP), tri-n-butylphosphate (TBP), benzyl acetate (BA), dioctylphthalate (DOP), *o*-nitrophenyloctyl ether (*o*-NPOE), tetrahydrofuran (THF) potassium carbonate (K_2CO_3) and high molecular weight poly(vinylchloride) were purchased from E. Merck (Germany) and used as received. Salicylaldehyde, 1,3-dibromo-propane, 3,4-diaminotoluene and methylacrylate were procured from Aldrich (USA). The nitrate and chloride salts of all the cations used were of analytical grade and used without any further purification. The solutions of metal salts were prepared in doubly distilled water and standardized whenever necessary.

2.2. Synthesis of 1,4-bis(2-carboxyaldehydephenoxy)butane

To a stirred solution of salicylaldehyde (0.02 mol L^{-1}) and K_2CO_3 (0.01 mol L^{-1}) in DMF (100 mL) was added dropwise 1,3-dibromopropane (0.01 mol L^{-1}) in DMF (40 mL) [29]. The reaction was continued for 10 h at 150–155 °C and then 5 h at room temperature. A 200 mL distilled H_2O was then added and the reaction mixture was kept in a refrigerator. Then 1 h later the precipitate was filtered and washed with 500 mL H_2O. It was then dried in air, recrystallised from EtOH and filtered under vacuum (Scheme 1). Yield: 16.7 g, M. pt.: 107–109 °C, color: bright brown. Anal calcd. for [$C_{17}H_{16}O_4$] (%): C, 71.82, H, 5.67, O, 22.51. Observed (%): C, 71.63, H, 5.53, O, 22.84%. ^{1}H NMR (MeOH, 500 MHz) δ_{ppm}: 7.06–7.72 (m, H–Ar, 8H), 2.32–2.38 (m, –C–CH$_2$–C–, 2H), 4.12–4.14 (t, –O–CH$_2$–C–, 4H), FT-IR (KBr, cm^{-1}): 3100 m(Ar–CH), 2962, 2880 (Aliph. –CH), 1670 (C=O), 1492, 1452 (Ar–C=C), 1280, 1242 (Ar–O).

2.2.1. Synthesis of macrocyclic ligand 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene-9,12-N$_2$-1,5-O$_2$ (L_1)

The macrocyclic ligand (L_1) was prepared by the dropwise addition of a solution of 3,4-diaminotoluene (0.01 mol L^{-1}) in MeOH (40 mL) to a stirred solution of 1,4-bis(2-carboxyaldehydephenoxy)butane (0.01 mol L^{-1}) in MeOH (60 mL). After the addition was completed, the stirring was continued for 4 h. A resulting yellow compound was filtered. Then, CH_2Cl_2 was added to the filtered compound which dissolved. Then, the solution was filtered and n-hexane was added to the filtered solution. A yellow compound was obtained and filtered (Scheme 2). M. pt.: 160 °C. Anal calcd. for [$C_{24}H_{22}N_2O_2$] (%): C, 77.81, H, 5.99, N, 7.56, O, 8.64. Observed (%):C, 77.83, H, 6.01, N, 7.52, O, 8.64. ^{1}H NMR (MeOH, 500 MHz) δ_{ppm}: 7.02–8.20 (m, H–Ar, 11H), 8.22 (s, CH=N, 2H), 2.24 (s, –CH$_3$, 3H), 2.30–2.37 (m, –C–CH$_2$–C–, 2H), 4.11–4.13 (t, –O–CH$_2$–C–, 4H), FT-IR (KBr, cm^{-1}): 3052 (Ar–CH), 2940, (Aliph. –CH), 1692 (C=N), 1496, 1460 (Ar–C=C), 1276, 1240 (Ar–O).

2.2.2. Synthesis of macrocyclic ligand 6,7:14,15-Bzo$_2$-10,11-(4-methylbenzene)-[15]-6,14-diene-9,12-dimethylacrylate-9,12-N$_2$-1,5-O$_2$ (L_2)

The macrocyclic pendant ligand L_2 was synthesized from macrocycle L_1 (Scheme 2). To a stirred solution of the macrocycle L_1 (1 mmol) in 10 mL saturated solution of anh. K_2CO_3 in anhydrous MeOH, 5 mL methylacrylate (excess amount) was added drop by drop and then it was stirred overnight and refluxed for 24 h. Then the volume was reduced half of its initial amount and was kept in a refrigerator overnight. A creamish colored oily product was obtained. Anal. calcd. for [$C_{32}H_{38}N_2O_6$] (%): C, 70.31; H, 7.01; N, 5.12; O, 17.56; Observed (%): C, 70.33; H, 7.00; N, 5.10; O, 17.57. ^{1}H NMR (MeOH, 500 MHz) δ_{ppm}: 7.04–8.22 (m, H–Ar, 11H), 2.30 (s, –CH$_3$, 3H), 2.31–2.37 (m, –C–CH$_2$–C–, 2H), 4.10–4.12 (t, –O–CH$_2$–C–, 4H), 2.48 (s, –N–CH$_2$–Ar–, 4H), 3.65–3.67 (t, –N–CH$_2$–C–, 4H), 4.62–4.64 (t, –C–CH$_2$–COOMe, 4H), 3.82 (s, OCH$_3$, 6H), FT-IR (KBr, cm^{-1}): 3050 (Ar–CH), 2945 (Aliph. –CH), 1490, 1455 (Ar–C=C), 1285, 1245 (Ar–O), 1740 (ester C=O str.), 1160 (OC–OCH$_3$ str.), 1121 (–OCH$_3$ str.).

2.3. Electrode preparation

The membranes have been fabricated as suggested by Craggs et al. [30]. Varying amount of the ion-active phase and anion excluder KTpClPB and NaTPB were dissolved with an appropriate amount of PVC in 3 mL THF. To these, solvent mediators, *viz.* DBP, TBP, *o*-NPOE, DOP and BA were added to get membranes of different compositions. The mixture was shaken vigorously with a glass rod. When the solution became viscous it was poured in acrylic ring placed on smooth glass plate. The solution was then allowed to evaporate for 24 h at room temperature. Transparent membranes of about 0.1 mm thickness were obtained, which were then cut to size and glued to one end of a Pyrex glass tube with araldite.