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On the potentiometric response of mercury(II) membrane sensors based on symmetrical thiourea derivatives—Experimental and theoretical approaches

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ABSTRACT

Mercury(II) sensors based on two bis-thioureas: 4,4′-bis-(3-phenylthiourea)diphenyl methane (L_1) and 2-2-[10-[(E)-2-(aminocarbothioyl)hydrazono]-1,4-dihydroxy-9(10H)-anthracenyliden]-1 hydrazinecarbothioamide (L_2) were prepared and studied. The best response characteristics were obtained using the composition—L_2:KTpClPB:PVC:DOP in the percentage ratio of 3.5:1.5:32:63 (w:w). The electrode exhibited a near Nernstian response of 30.3 mV decade^{-1} to mercury ions over the activity range 1.0×10^{-7} to 1.0×10^{-2} M with a limit of detection 7.9×10^{-8} M. The pH independent plateau ranges between 1.5 and 4.0. The proposed sensor revealed fairly good discriminating ability toward Hg^{2+} ion in comparison with many hard and soft metal ions. It could be applied to determination of mercury in waste water as a real sample. Besides, theoretical calculations performed using the Gaussian 09 programs indicate a S atom is the most favorite reactive site and mainly responsible for the observed electrochemical behaviors in Hg(II)-selective electrodes toward the different cations.

1. Introduction

Currently, there is an increasing demand to selectively sense heavy metal ions such as Hg(II), Cu(II) and Pb(II) because of their high toxicity [1,2]. Among these, Hg(II) can severely damage the kidneys and the gastrointestinal tract, and is generally a serious hazard to human health [3]. It is considered by the Environmental Protection Agency (EPA) as a highly dangerous element because of its accumulative and persistent character in the environment and biota [4]. It would cause a neurological damage, have a teratogenic effect, and even result in death [5]. This element poses human risks even at trace concentration levels. Therefore, the determination of mercury ion in environmental samples calls for highly sensitive, selective and rapid methods. It is well known that ion-selective electrode (ISE) is one of the few techniques that can measure both positive and negative ions and widely used in medical, biological and environmental investigation. The interest in ISEs have grown over recent years as they are portable, easy, and can provide accurate rapid measurements with reasonable sensitivity and selectivity [6,7]. A frequently encountered type of ISE is a solvent polymeric membrane electrode. Commonly encountered ISEs of this type are polyvinyl chloride (PVC)-based membrane electrodes prepared from PVC, a plasticizer, an ionophore and other components. The key feature of the sensitive sensor membrane is the incorporated carrier, which is a sensitive and selective compound that recognizes the target ion, giving an adequate electrochemical response. The recognition depends, ultimately, on the nature of the chemical bond that is formed between the ionophore and the metallic ion. However, little is known about the bonding originated from the interaction of heavy metal ions with ionophores. Nowadays, many ligands have been investigated as ionophores, including crown ethers [8,9], calixarenes [10,11] and Schiff base derivatives [12–14]. Considerable work has proved the fact that nitrogen and sulfur atoms contained in compounds promote the coordination of compounds with heavy metal ions [15,16]. The selectivity behavior of the carrier to the analyzed ion has been explained on the molecular recognition basis [17]. Within this framework, several ideas and models have been proposed to understand the mechanism of the membrane response [18]. As described by the hard–soft acid base (HSAB) concept, a so-called “soft” acid such as a transition metal ion and a sulfur atom as a “soft” base often form a strong coordination bond between them. For this reason, sulfur atom-containing molecules often form a very stable complex with a transition metal ion; hence,

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reversible potentiometric response to the transition metal ion is not obtained when such a molecule is used as the ion-sensing material for an ion-selective electrode [19]. Many compounds containing S atom have been successfully used as ionophores for mercury ion-selective electrode and verified the possibility by means of density functional theory calculations [18,20]. Therefore, we were prompted to investigate the behavior of two sulfur-containing ligands, 4,4′-bis-(3-phenylthiourea)diphenyl methane (L_1, Fig. 1a) and 2-2-[10-[(E)-2-(aminocarbothioyl)hydrazono]-1,4-dihydroxy-9(10H)-anthracenyliden]-1 hydrazinecarbothioamide (L_2, Fig. 1b) as mercury ionophores. Also, the electrode characteristics of the optimized mercury(II)-selective electrodes were studied in detail. Besides, in the present study, we will provide a theoretical approach that may give insight, at the molecular level, into the recognition properties that are exhibited by these types of selective carriers. This approach could facilitate the prediction of the fitness of the molecular recognition capability of such molecular structure. At the same time, this type of theoretical approach may save time and many trial and error experiments. Thus, quantum chemical parameters such as highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE) and softness (σ) were calculated for these compounds by using ab initio theoretical calculations. Finally, we will attempt to rationalize the observed reactivities in terms of the HOMO–LUMO energy difference, namely hardness and softness. The results of our study may provide contributions toward the prediction of the applicability of the material design of metal ion recognition and related fields.

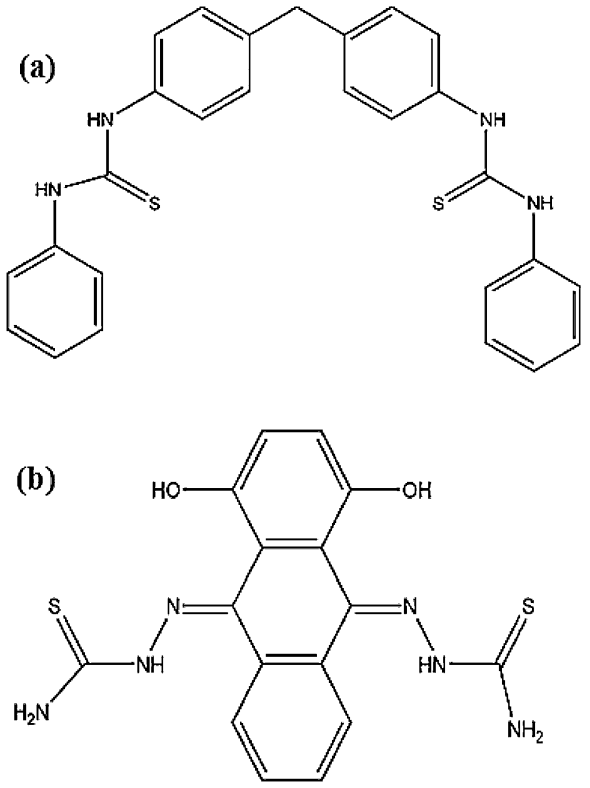

Fig. 1. (a) Bis-thioureas: 4,4′-bis-(3-phenylthiourea)diphenyl methane (L_1). (b) Structure of ionophore 2-2-[10-[(E)-2-(aminocarbothioyl)hydrazono]-1,4-dihydroxy-9(10H)-anthracenyliden]-1 hydrazinecarbothioamide (L_2).

2. Experimental

2.1. Reagents

All of the reagents used were of analytical-reagent grade. For membrane preparation, high molecular weight poly(vinyl chloride) (PVC), dibutyl phthalate (DBP), dioctyl phthalate (DOP), o-nitrophenyl octyl ether (o-NPOE) and potassium tetrakis (p-chlorophenyl) borate (KTpClPB), tetrahydrofuran (THF) were used as received from Merck or Fluka. The sample solutions used for potentiometric measurements were prepared by dissolving their nitrate salts in double distilled water and standardized wherever necessary.

2.2. Ionophore synthesis

2.2.1. Synthesis of 4,4′-bis-(3-phenylthiourea)diphenyl methane (L_1)

The ionophore 4,4′-bis-(3-phenylthiourea)diphenyl methane (L_1) was prepared according to the literature methods [21]. 4,4′-Diaminophenylmethane (0.5 g, 0.005 mol) and phenyl isothiocyanate (0.68 g, 0.01 mol) were treated in dry 1,4-dioxane and dichloromethane (25 mL) at room temperature for 12 h. The white precipitate of the product formed was filtered through a sintered funnel and then washed thoroughly with 1,4-dioxane and dichloromethane in order to remove any substrate impurity. Anal. Calc. for [$C_{27}H_{24}N_4S_2$]: C = 69.20; H = 5.16; N = 11.96; Found: C = 69.01; H = 5.32; N = 11.88%. ^{1}H NMR (400 MHz, DMSO-d_6): 9.70 (s, 2H, NH), 9.69 (s, 2H, NH), 7.47–7.11 (m, 16H), 3.88 (s, 2H).

2.2.2. Synthesis of 2-[10-[(E)-2-(aminocarbothioyl)hydrazono]-1,4-dihydroxy-9(10H)-anthracenyliden]-1 hydrazinecarbothioamide (L_2)

The anthracene-based thiourea (ionophore) was synthesized in the organic laboratory according to the following procedure. The stirred solution of 1,4-Dihydroxyanthraquinone (0.01 M in absolute methanol) was added a solution of thiosemicarbazide (0.02 M in absolute methanol). The contents were refluxed for 14 h (in the presence of a small amount of concentrated hydrochloric acid), and then cooled to room temperature. The solid product was filtered and recrystallized from choloroform. The resulting precipitate was characterized and used for the next step. Yield (65%), color: brownish, mp: 233–235 °C. The ^{1}H NMR (400 MHz, DMSO-d_6) exhibited signals at: δ 5.1 (s, 2H, OH), 7.2 (s, 2H, NH), 1.9 (bs, 4H, NH_2), 7.4–7.9 (m, 4H, Ar–H), 6.9 (s, 2H, Ar–H). Elemental analysis % observed for [$C_{16}H_{14}N_6O_2S_2$]: C = 49.7; H = 3.6; N = 21.7; S = 16.6; O = 8.3 (%). Found: C = 49.6; H = 3.7; N = 21.9; S = 16.5; O = 8.4 (%).

2.3. Potentiometric measurements

All potentiometric measurements were performed at 25 ± 1 °C using a 713 pH mV meter (Metrohm Co., Herisau, Switzerland) with an Orion Ag/AgCl double-junction electrode. The experimental solution was stirred with a stirring bar at 120 min^{-1} and potential readings recorded when they reached steady state values. In all cases, a 1.0×10^{-2} M HNO_3 solution was used as electrolyte medium. Diagrammatic sketch of a measurement by ion-selective electrode is illustrated in Fig. 2.

The representative electrochemical cell for the emf measurements was as follows:

Ag/AgCl | 3 M KCl | salt bridge (1 M KNO_3) | test solution | PVC membrane | inner filling solution (1×10^{-3} M $Hg(NO_3)_2 + 1 \times 10^{-2}$ M HNO_3) | 1 M KCl | Ag/AgCl