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Response characteristics of Dy³⁺ ion selective electrodes based on N,N'-bis(naphthalidene)-2-aminobenzylamine

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ABSTRACT

It was found that N,N'-bis(naphthalidene)-2-aminobenzylamine (BNA) containing PVC membranes display a good Dy(III) selectivity in comparison to most common first and second main group elements (representative), transition, and lanthanide ions. Therefore, we investigated its use as an neutral ion carrier, for preparing a Dy(III) PVC-membrane electrode. The primarily studied PVC-based membranes contained sodium tetraphenyl borate (NaTPB) as an anionic additive, and were tested by using different solvent mediators such as benzyl acetate (BA), nitrobenzene (NB), and dibutyl phthalate (DBP). The effects of the membrane composition, pH, and additive anionic influence on the response properties were investigated. The best performance was obtained with a membrane containing 30% PVC, 66% NB, 2% BNA, and 2% NaTPB. The electrode shows a Nernstian behavior (slope of 20.7 ± 0.4 mV per decade) over a very wide iron ion concentration range (1.0×10^{-6} - 1.0×10^{-2} M) and has a low detection limit (5.2×10^{-7} M). The potentiometric response of the sensor is independent of pH of the solution in the pH range 2.5–8.6. The proposed sensor has a very low response time (~7 s).

Keywords: Potentiometry, PVC Membrane, Sensor, Ion-Selective Electrode.

INTRODUCTION

The utility of ion-selective electrodes (ISEs) is being increasingly realized by analytical chemists in view of the rapid growth of industry and technology all over the world as they represent a rapid, accurate and low-cost method of analysis. Determination of rare earth compounds is considered necessary because of their applications in bioinorganic and inorganic chemistry, industrial use and also their enhanced discharge, toxic properties and other adverse effects. Dysprosium, a rare earth element that has a metallic, bright silver luster, is relatively stable in air at room temperature but dissolves readily in dilute or concentrated mineral acids with the emission of hydrogen. Dysprosium is widely used in fluorescence material, magnetic material,

and life science experiments [1]. The commonly methods for low-level detection of Dy^{3+} ions in solutions are spectrophotometry, ion mass spectroscopy and higher order derivative spectrometric procedure and preconcentrative ICP-MS and neutron activation analysis (NAA), etc. These methods are either time consuming, involve multiple sample manipulations or are too expensive for most analytical laboratories. Potentiometric membrane sensors have been shown to be very effective tools for the analysis of a wide variety of metal ions. They are very simple, fast, inexpensive and capable of reliable response in wide concentration ranges [2]. Recently, a number of polyvinyl chloride (PVC)-membrane sensors were reported for alkaline earth, transition metal ions [3-27]. In this research, we wish to report the preparation of a Dy^{3+} PVC-based membrane electrode based on *N,N'*-bis(naphthalidene)-2-aminobenzylamine (BNA) as an neutral ion carrier.

EXPERIMENTAL SECTION

Reagent grade acetophenone (AP), dibutyl phthalate (DBP), nitrobenzene (NB), benzylacetate (BA), sodiumtetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight PVC were purchased from Merck and Aldrich and used as received. The ionophore BNA was synthesized as described elsewhere [28-31]. The nitrate and chloride salts of all cations used (all from Merck and Aldrich) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5 . Triply distilled de-ionized water was used throughout the experiments.

To prepare the PVC membrane a thoroughly mixed mixture comprising 30 mg of powdered PVC, 66 mg of plasticizer NB, 2 mg of additive NaTPB, and 2 mg of ion carrier BNA, in 5 mL of fresh THF, was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3–5mm o.d.) was dipped into the mixture for about 5 s to form a transparent membrane of about 0.3mm thickness on its tip. The tube was then pulled out and kept at room temperature for about 12 h, before being filled with the internal filling solution (1.0×10^{-3} M of DyCl_3) [32-34]. The membrane sensor was finally conditioned by soaking in a 1.0×10^{-3} M DyCl_3 solution for 24 h. A silver/silver chloride wire was used as an internal reference electrode.

All electromotive force (emf) measurements were carried out with the following cell assembly:
 $\text{Ag-AgCl} \mid \text{internal solution, } 1.0 \times 10^{-3} \text{ M } \text{DyCl}_3 \mid \text{PVC membrane} \mid \text{test solution} \mid \text{Hg-Hg}_2\text{Cl}_2, \text{KCl (satd.)}$

A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0 °C. The activities were calculated according to the Debye–Hückel procedure.

RESULTS AND DISCUSSION

The existence of two donating oxygen and nitrogen atoms in the ionophore (BNA) was expected to increase both the stability and selectivity of its complexes with transition and heavy metal ions as soft acids, more than other metal ions. Thus, in preliminary experiments, the BNA was used as a potential neutral carrier in construction of PVC membrane ion selective electrodes for Dy(III) ion. The potential response obtained for this cation clearly exhibited that the resulting Dy^{3+} -selective electrode possesses a Nernstian behavior over a very wide concentration range.

Several important features of the PVC membranes, such as the properties of the plasticizer, the plasticizer/PVC ratio, the nature and amount of ionophore, and especially the nature and amount

of the additive used are reported to influence the sensitivity and selectivity of the ion-selective electrodes significantly. In general, the presence of lipophilic anions in cationselective membranes based on a neutral carrier not only diminishes the ohmic resistance and enhances the response behavior and selectivity, but also, in cases where the extraction capability is poor, increases the sensitivity of the membrane electrodes [35–41]. Thus, different compositions of the Dy(III)-selective membrane were optimized, and the results are given in Table 1. Obviously, from Table 1, the sensor slope in the absence of sodium tetraphenyl borate (NaTPB) is lower than the expected Nernstian value (membrane no. 1). Nevertheless, the addition of 2% NaTPB will increase the sensitivity of the electrode response considerably, so that the membrane electrode demonstrates a Nernstian behavior (membrane no. 3). However, the membranes with the composition of 30% PVC, 2% BNA, 2% NaTPB and 66% nitrobenzene (NB) exhibit a Nernstian potential response. Among four different solvent mediators tested, NB is superior with respect to dibutyl phthalate, benzyl acetate and acetophenone. All the used plasticizers have a nearly low donocity number (DN) but different dielectric constants (DC). NB is used as a plasticizer because of having a higher dielectric constant than the others. The higher DC of NB helps the better extraction of the polar Dy(III) ion, which is a cation with high charge density from the aqueous layer to the organic layer of the membrane and causes a better and faster response.

The emf response of the membrane at varying activity of Dy^{3+} (Fig. 1) indicates a rectilinear range from 1.0×10^{-6} to 1.0×10^{-2} M. The slope of the calibration curve was 20.7 ± 0.4 mV per decade of Dy^{3+} concentration. The limit of detection of the proposed sensor, as determined from the intersection of the two extrapolated segments of the calibration graph, was 5.2×10^{-7} M.

Table 1: Optimization of membrane ingredients of the Dy^{3+} ion-selective electrode based on BNA

Sensor No.	Composition (wt%)				Slope (mV decade ⁻¹)	Concentration range (M)
	BNA	NaTPB	Plasticizer	PVC		
1	2	0	NB, 68	30	14.1 ± 0.3	1.0×10^{-5} - 1.0×10^{-2}
2	2	1	NB, 67	30	17.9 ± 0.7	1.0×10^{-6} - 1.0×10^{-2}
3	2	2	NB, 66	30	20.7 ± 0.4	1.0×10^{-6} - 1.0×10^{-2}
4	2	3	NB, 65	30	19.1 ± 0.6	1.0×10^{-6} - 1.0×10^{-2}
5	1	2	NB, 67	30	15.6 ± 0.5	1.0×10^{-5} - 1.0×10^{-2}
6	3	2	NB, 65	30	18.4 ± 0.2	1.0×10^{-6} - 1.0×10^{-2}
7	2	2	AP, 66	30	18.8 ± 0.6	1.0×10^{-6} - 1.0×10^{-2}
8	2	2	DBP, 66	30	14.1 ± 0.3	1.0×10^{-6} - 1.0×10^{-2}
9	2	2	BA, 66	30	16.4 ± 0.5	1.0×10^{-6} - 1.0×10^{-2}

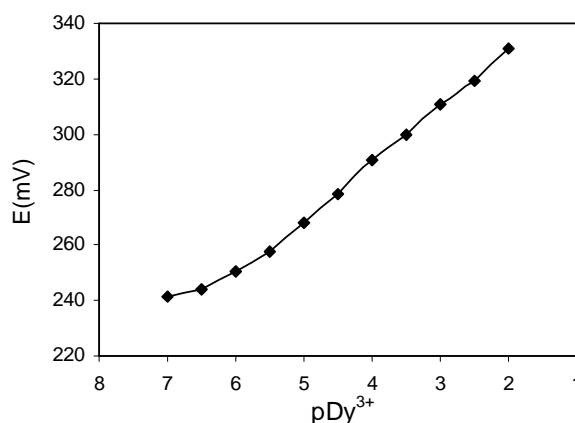


Figure 1. Calibration curve of Dy(III) electrode based on BNA.

The potential response of the electrode was considered in the pH range of 1.0–11.0 (the pH was adjusted by using concentrated NaOH or HCl) and the results are depicted in Figure 2. As seen, the potential response of the sensor remains constant in the pH range of 2.5 – 8.6.

For analytical applications, dynamic response time is very important for any sensor. The dynamic response time of the membrane was measured at various concentrations (1.0×10^{-6} to 1.0×10^{-2} M) of the test solutions and the results are illustrated in Figure 3. As it can be seen, in the whole concentration range the electrode reaches its equilibrium response, very fast (~ 7 s).

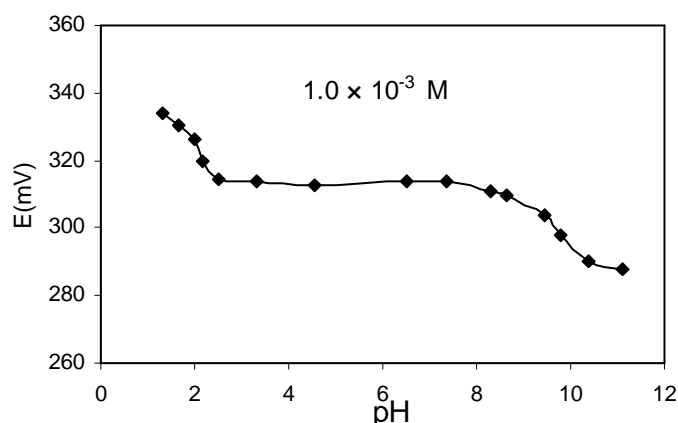


Figure 2. pH effect of the test solution (1.0×10^{-3} M of Dy^{3+}) on the potential response.

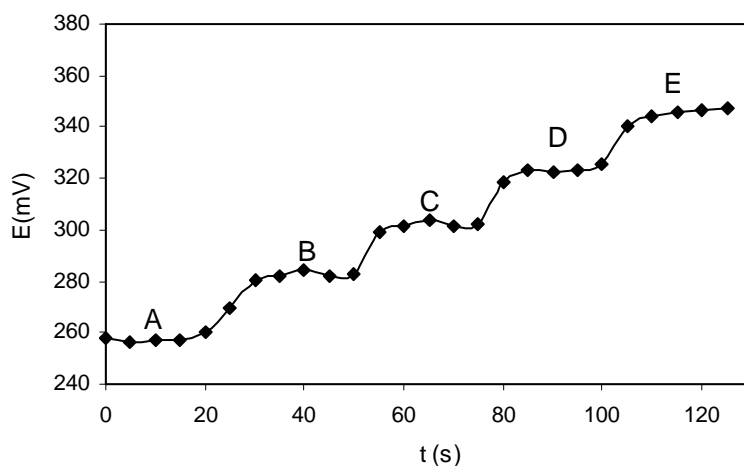


Figure 3. Dynamic response time of the Dy^{3+} electrode for step changes in the Dy^{3+} concentration: A) 1.0×10^{-6} M, B) 1.0×10^{-5} M, C) 1.0×10^{-4} M, D) 1.0×10^{-3} M, E) 1.0×10^{-2} M.

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