



Dysprosium(III) polyvinyl chloride membrane sensor: A study of interfering ions effect on efficiency of sensor

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ABSTRACT

A PVC membrane sensor for dysprosium(III) ions based on *N,N'*-bis(naphthalidene)-2-aminobenzylamine (BNA) as a suitable ionophore with a linear dynamic range of 1.0×10^{-6} - 1.0×10^{-2} M, a Nernstian slope of 20.7 ± 0.4 mV per decade, a detection limit of 5.2×10^{-7} M, pH range of 2.5–8.6 and response time of ~ 7 s was constructed. In this research, on the fabricated electrode, the potential responses of the recommended Dy(III) membrane sensor to a wide variety of cations were investigated through the matched potential method (MPM). The recommended sensor revealed comparatively good selectivity with respect to most alkali, alkaline earth, some transition, and heavy metal ions. It was successfully employed as an indicator electrode in the potentiometric titration of Dy(III) ions with EDTA.

Keywords: Ion selective electrode, Potentiometry, Sensor, PVC membrane.

INTRODUCTION

Dysprosium is widely used in fluorescence material, magnetic material, and life science experiments. Identifying a sensitive and reliable method of determination is very important. Dy(III) has already been determined, in the presence of other rare earth elements, by some non-electrochemical methods such as spectrometry and inductively coupled plasma method. But all of these methods are expensive and need complicated equipment. Potentiometry using ion-selective electrodes is a fast, ease of preparation and procedure, simple instrumentation, very low detection limit, wide dynamic ranges, inexpensive, and simple method for determination of ions. This has led to increasing the number of available electrodes over the last few years [1, 2]. According to the experiences of our team and other researchers in construction of selective and

sensitive polyvinyl chloride membrane sensors for various metal ions [3–18], we decided to assess the potentials of using N,N'-bis(naphthalidene)-2-aminobenzylamine (BNA) (Fig. 1) as an ionophore for constructing a highly selective Dy³⁺-selective sensor that can be used in real time analysis of this element.

EXPERIMENTAL SECTION

Reagents

Reagent grade nitrobenzene (NB), dibutyl phthalate (DBP), acetophenone (AP), benzyl acetate (BA), sodium tetraphenylborate (NaTPB), tetrahydrofuran (THF), and high relative molecular weight PVC were purchased from Merck and Aldrich, used as received. The ionophore BNA was synthesized as described elsewhere [19-22]. 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 P₂O₅. Triply distilled, de-ionized water was used throughout.

EMF measurements

All electromotive force (emf) measurements were carried out with the following cell assembly; Ag–AgCl | 1.0×10⁻³ M DyCl₃ | PVC membrane: test solution | Hg–Hg₂Cl₂, KCl (satd).

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

Electrode preparation

The general procedure to prepare the PVC membrane was to mix thoroughly, 30 mg of PVC, 66 mg nitrobenzene (NB) and 2 mg of NaTPB in 5 mL THF. To this solution was added 2 mg of BNA and the combination was mixed well. The resulting mixture was transferred into a glass dish of 2 cm diameter. A Pyrex tube (5 mm o.d.) was dipped into the mixture for about 5 s so that a nontransparent membrane (about 0.3 mm thickness) is formed. The tube was then pulled out from the mixture and kept at room temperature for at least 12 h. The tube was then filled with internal filling solution (1.0 × 10⁻³ M DyCl₃). The electrode was finally conditioned for 24 h by soaking in a 1.0 × 10⁻³ M DyCl₃ [23-35]. A silver/silver chloride electrode was used as an internal reference electrode.

RESULTS AND DISCUSSION

The ionophore BNA was used as a neutral carrier to prepare the Dy(III) PVC ion-selective membrane sensor. The membrane composition and, especially in some cases, the nature of the additive have a significant influence on the sensitivity and selectivity for a certain ionophore. Also, the presence of lipophilic and immobilized ionic additives could influence the membrane resistance and, sometimes, the selectivity pattern of the ion-selective PVC membrane, resulting in a good working performance [36, 37]. The membrane sensor with composition of 30% PVC; 66% NB; 2% NaTPB, and 2% BNA exhibits the best performance.

One of the most important characteristics of a cation-selective membrane electrode is its relative response towards one ion over other ions present in the solution, which is usually expressed in

terms of potentiometric selectivity coefficients. For the selectivity coefficient measurements, the matched potential method was used. According to the MPM [38, 39], a specified activity (concentration) of primary ions (A) is added to a reference solution and the potential is measured. In a separate experiment, interfering ions (B) are successively added to an identical reference solution, until the measured potential matches that obtained before the primary ion addition. The MPM selectivity coefficient is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K^{MPM} = a_A/a_B$. The experimental conditions and the resulting values are listed in Table 1. For all the tested ions, the selectivity coefficients were of the order 6.3×10^{-3} or smaller, indicating that they would not radically disturb the function of the sensor. Therefore, the electrode may be used for Dy(III) ion detection in the presence of certain interfering ions. The characteristics of the sensor were compared with those of the best Dy(III) electrodes reported in the literature [40, 41] (Table 2). It can be concluded that this sensor in terms of selectivity, detection limit, response time and dynamic concentration range, was superior to all previously described Dy(III) sensors.

Table 1: Selectivity coefficients of various interfering ions

Interfering ion (B)	Selectivity coefficient (MPM)
Ho ³⁺	5.3×10^{-4}
Tb ³⁺	7.4×10^{-4}
Pr ³⁺	6.1×10^{-4}
Lu ³⁺	4.6×10^{-3}
Yb ³⁺	2.5×10^{-3}
Eu ³⁺	1.0×10^{-3}
Gd ³⁺	5.7×10^{-4}
Cr ³⁺	5.8×10^{-4}
Al ³⁺	8.3×10^{-4}
Na ⁺	5.6×10^{-4}
K ⁺	6.1×10^{-4}
Ca ²⁺	4.3×10^{-4}
Mg ²⁺	7.2×10^{-4}
Ba ²⁺	6.5×10^{-4}
Cu ²⁺	7.6×10^{-4}
Cd ²⁺	5.9×10^{-3}
Pb ²⁺	6.3×10^{-3}

Table 2: Comparison of the selectivity coefficients, linearity range, detection limit and response time of proposed Dy(III) electrode and the previously reported Dy(III) PVC-membrane sensors

Character / reference	Ref. 40 (MPM)	Ref. 41 (MPM)	This work (MPM)
Log $K_{sel} > -2$	La ³⁺ , Ce ³⁺ , Gd ³⁺ , Sm ³⁺ , Yb ³⁺	—	—
Response time (s)	<20	<10	~7 s
Linearity range (M)	1.0×10^{-5} - 1.0×10^{-1}	8.0×10^{-7} - 1.0×10^{-1}	1.0×10^{-6} - 1.0×10^{-2}
Limit of detection (M)	6.0×10^{-6}	4.2×10^{-7}	5.2×10^{-7}

The Dy(III) membrane electrode was found to work well under laboratory conditions. It was successfully applied to the titration of a Dy(III) solution with EDTA. The resulting titration curve is displayed in Fig. 2, where it can be observed that the Dy(III) amount in solution can be accurately detected.

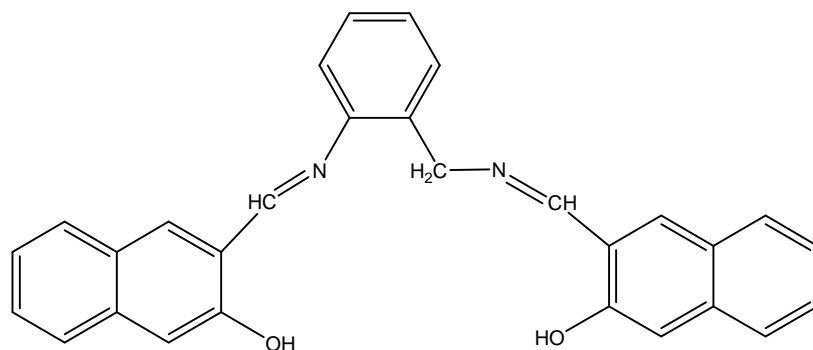


Figure 1. The BNA chemical structure

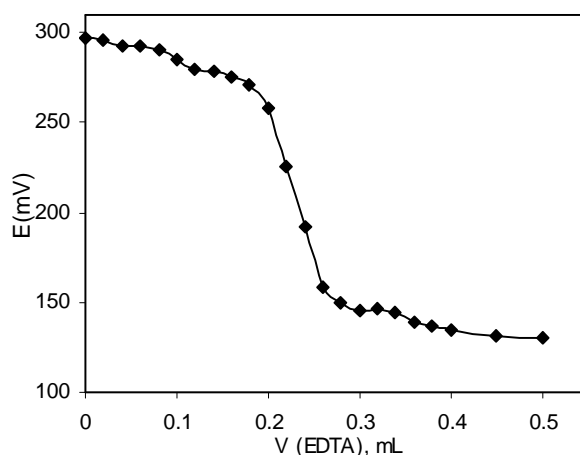


Figure 2. Potential titration curve of 25.0 mL from a 1.0×10^{-4} M Dy^{3+} solution with 1.0×10^{-2} M of EDTA

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