GRAPHITE COATED BARIUM (II) SELECTIVE MEMBRANE ELECTRODE BASED ON DIBENZO24-CROWN-8

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ABSTRACT

A graphite coated electrode for the selective determination of barium ion on a PVC matrix using dibenzo-24-crown-8 as ionophore is reported. The sensor illustrated a linear dynamic range of 1.0 x 10^{-6} to 1.0 x 10^{-3} M, a Nernstian slope of 30.1mV/decade, a detection limit of 6.1 × 10^{-7} M and a response time of <10s. The electrode showed no significant change in potential in the pH range of 4.1 - 9.0. Fabricated electrode exhibited good selectivity with respect to other cations as determined by the matched potential method. The fabricated electrode was used as an indicator electrode in the potentiometric titration of Ba(II) with EDTA.

Key words: Ion – selective electrode, graphite, barium, dibenzo24crown8, potentiometry, PVC membrane

1. INTRODUCTION

Barium, an important alkaline earth metal finds application in the plastics, rubber, electronics and textile industries, in ceramic glazes and enamels [1], in glass-making, brick-making and paper-making, as a lubricant additive, in pharmaceuticals and cosmetics, in case-hardening of steel and in the oil and gas industry as a wetting agent for drilling mud. Barite (barium sulphate) is the most common mineral of barium. It is colorless or white, often tinged with yellow, brown, red or bluish and used in the production of wallpaper and asbestos goods as well as in the manufacture of white paint. The principal use of barite is as a weighting agent in oil and natural gas drilling [2]. Its short term exposure can cause vomiting, abdominal cramps, diarrhea, difficulties in breathing, numbness around the face, and muscle weakness. Large amounts of barium intake can cause high blood pressure, changes in heart rhythm or paralysis and possible death in certain cases [3]. It was important to develop a selective and sensitive method for determination of Ba(II) because of its wide applications mentioned above.

Certain time-consuming and laborious techniques are developed for the determination of Ba(II) such as Atomic Absorption Spectrometry (AAS) [4], Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) [5], X-ray Fluorescence spectrometry [6], etc. All required multiple steps for sample preparation and also quite expensive for most analytical laboratories. Several metal ions have been studied by using various macrocyclic ligands as ionophores [7-11]. Crown ethers can form host-guest complexes with many metal ions, particularly with alkali and alkaline earth metals [12]. According to literature Ba(II) forms stable complex with dibenzo-24-crown-8 (DB24C8) [13-15]. Coated graphite ion-selective electrodes have been admired because they are very simple, durable, inexpensive and offers reliable response over a wide concentration range [16, 17].

Therefore, it was important to develop a graphite coated electrode for the selective determination of Ba(II).

2. EXPERIMENTAL

2.1 Reagents

Analytical grade barium nitrate, sodium tetraphenyl borate (NaTPB), dibutyl phthalate (DBP), dibutyl maleate (DBM) was obtained from Loba Chemie. High purity dibenzo24crown8 (DB24C8), o-nitrophenyl octylether (o-NPOE) were obtained from Chemical Centre, Multiwalled carbon nanotube was obtained from Sigma-Aldrich while tetrahydrofuran (THF) and polyvinyl chloride (PVC) were obtained from SD fine Chemicals and Chemical International respectively.

2.2 Fabrication of electrode

A homogenous paste was made by mixing polymer matrix (PVC) with varying amounts of plasticizer (*o*-NPOE, DBP, DBM), anion excluder (NaTPB), MWNT and ionophore (DB24C8) in a small beaker. After addition of 3ml of tetrahydrofuran (THF) followed by sonication, the solvent was evaporated by rapid stirring until an oily concentrated mixture was obtained. A clean graphite electrode was then dipped into the mixture to get a uniform coating of the membrane on the electrode surface. Nine electrodes having different compositions were prepared in the same manner (**Table 1**). All the electrodes were dried under an IR lamp for 24 hours. After drying, the electrodes were conditioned by soaking them in a 1×10^{-3} M Ba(II) solution for 48 hours.

2.3 Electromotive Force (emf) Measurements

A digital dual channel Potentiometer Model (EQ-603) was used for the potential measurements. All the emf measurements were carried out using the following cell assembly

$$^{-}\text{SCE} \,|\, \text{x M Ba(II)solution} \,||\, \text{membrane} \,|\, \text{graphite}^{+}$$

The membrane electrode potential was measured against a reference saturated calomel electrode (SCE).

3. RESULTS AND DISCUSSIONS

DB24C8 was employed as a potentially suitable neutral carrier in the construction of the PVC membrane ion selective electrodes for Ba(II) ions. DB24C8 has the following structure

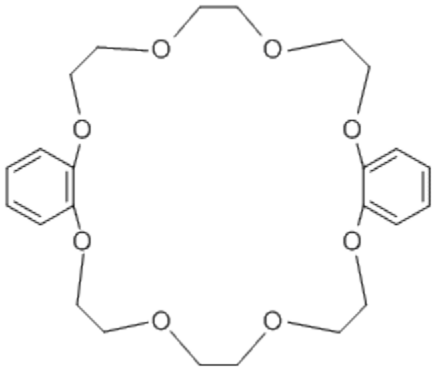

Figure 1 DB24C8 structure

3.1 Effect of membrane composition

The sensitivity, linear dynamic range and selectivity of the ion selective electrode (ISE) depend not only on the nature of the ionophore used but also significantly on the membrane composition and

the properties of the additives employed [18-24]. The performance characterstics of several membranes having ingredients of different proportions are summarized in **Table 1.**

No.	DB24C8 (%)	MWNT (%)	NaTPB (%)	DBP (%)	DBM (%)	*o*-NPOE (%)	PVC (%)	Working range (M)	Slope mV/decade
1	2.0	---	6.0	---	---	59.0	33	$10^{-5}$to 10^{-2}	19.4
2	**2.0**	**2.0**	**6.0**	**---**	**---**	**57.0**	**33**	**10^{-6} to 10^{-3}**	**30.1**
3	2.0	2.0	---	---	---	61.0	33	10^{-6} to 10^{-4}	23.0
4	4.0	4.0	6.0	---	---	53.0	33	$10^{-6}$to 10^{-4}	30.0
5	5.0	4.0	6.0	---	---	52.0	33	$10^{-6}$to 10^{-4}	20.0
6	6.0	4.0	6.0	---	---	51.0	33	$10^{-5}$to 10^{-3}	19.5
7	4.0	4.0	6.0	---	53.0	---	33	$10^{-5}$to 10^{-3}	20.0
8	4.0	4.0	6.0	53.0	---	---	33	$10^{-5}$to 10^{-3}	17.0
9	1.0	2.0	6.0	---	---	58.0	33	10^{-5} to 10^{-3}	22.5

Table1. Composition and response characteristics of Ba (II) selective graphite MWNT-PVC membrane electrode

Nature of the plasticizer influences the dielectric constant of the membrane and the mobility of ionophore and its complex [25]. The response of the electrode containing o-NPOE (Electrode No. 4), DBM (Electrode No. 7) and DBP (Electrode No. 8) as plasticizers were studied. It was found that the membrane containing o-NPOE as plasticizer with a high dielectric constant (24) and high polarity showed the best response. The response of the electrode was found to improve in presence of anion excluder NaTPB (Electrode No. 2 and 3). Literature suggested that the presence of lipophilic negatively charged additives such as NaTPB reduces the ohmic resistance, improves the response behavior and selectivity of the electrode [26-28]. The presence of nanotubes improved the response of the electrode to Nernstian values (Electrode No. 1 and 2) due to their high electrical and thermal conductivity, interesting properties such as an ordered structure with a high aspect ratio, high surface area. The best response characteristics were obtained for the membrane having composition of 33.0% PVC, 57.0% o-NPOE, 6.0% NaTPB, 2.0 % MWNT and 2.0% DB24C8.

3.2 Calibration graph

The plot of emf vs. pBa obtained for the electrode with optimum membrane composition (Electrode No. 2) indicated Nernstian behavior over a wide concentration range of Ba(II) ion. The slope and linear range of the resulting calibration graph were 30.1mV/decade and (1.0×10^{-6} to 1.0×10^{-3} M) respectively. The limit of detection, defined as the concentration of Ba(II) ion obtained when the linear regions of the calibration graph are extrapolated to the base line potential was 6.1×10^{-7} M. The developed electrode was stable and could be used for at least 3 months without any change in its response characteristic.

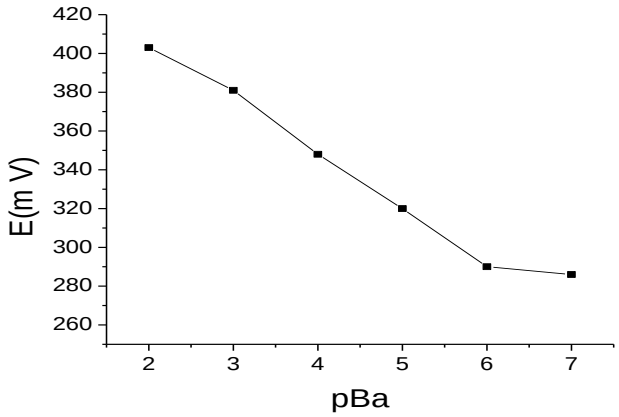

Figure 2 Calibration curve of graphite coated barium selective electrode

3.3 Effect of pH

The pH dependence of the developed electrode was tested over a pH range of 2.0 to 11.0 in a 1×10^{-4} M Ba(II) solution and the results obtained are illustrated in **Figure 3**. The potential was found to remain constant in the pH range of 4.1 – 9.0. Beyond this range, there was a gradual change in potential. At higher pH values, the potential decreased while at lower pH values, it increased. Response of the electrode indicates that the change in potential values depend on pH. Decrease in potential may be due to the formation of some OH^- complexes of Ba(II) while an increase in potential indicates that the membrane sensor now responds to H^+ ions.

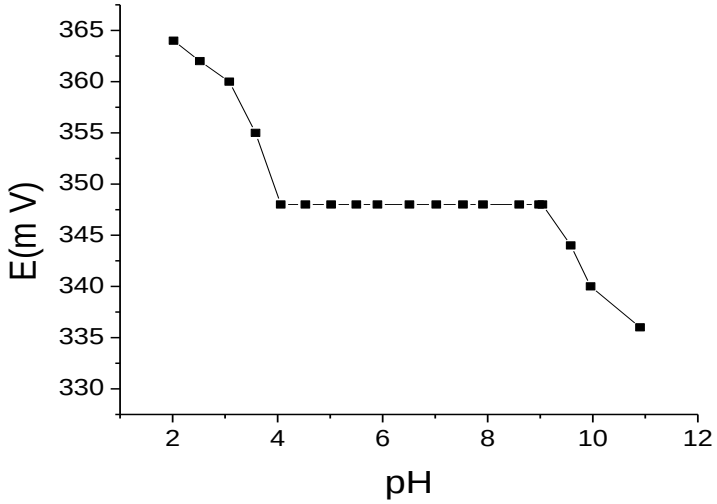

Figure 3 Effect of pH of test solution (1×10^{-4} M) on the potential response of barium sensor

3.4 Dynamic response time:

An ion exchange membrane leads to dynamic response time. For any ion-selective electrode response time is one of the most important factor. It is the average time required for the electrode to reach a potential within ± 1 mV of the final equilibrium value after successive immersions of a series of Ba(II) solutions, each having a 10-fold concentration difference [29]. In this study, the practical response time of the sensor was recorded by changing the concentration of Ba (II) over a

range of 1.0 x 10^{-6} to 1.0 x 10^{-3} M. The results obtained are shown in **Figure 4**. It was found that the electrode reaches its equilibrium response in a very short time (<10s).

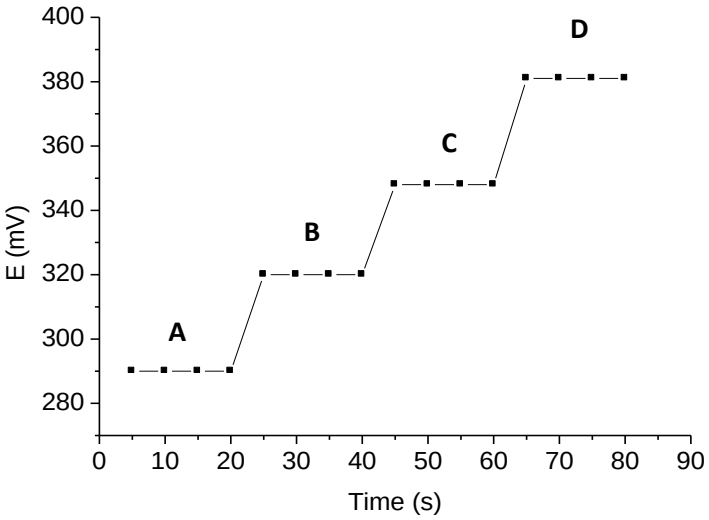

Figure 4 Dynamic response time of the barium selective electrode with step changes in concentration of Ba(II) (**A**: 1.0 x 10^{-6} M, **B**: 1.0 x 10^{-5} M, **C**: 1.0 x 10^{-4} M, **D**: 1.0 x 10^{-3} M)

3.4 Selectivity coefficient

The potentiometric selectivity coefficients which reflect the relative response of the membrane sensor for the primary ion over other ions present in the solution is perhaps the most important characteristic of an ion selective electrode. To investigate the membrane electrode selectivity, its potential response was monitored in the presence of various other ions by the matched potential method (MPM) [30,31]. According to MPM, a specified activity or concentration of primary ion (A) was added to a reference solution for its potential measurement. Separate experiment was carried out for interfering ions (B) that was further added to an identical reference solution until the measured potential matches the one obtained before by adding primary ions. The selectivity coefficient, $K_{A,B}$ is determined as

$K_{A,B} = \Delta A/A_B$

where $\Delta A = a'_A - a_A$, a_A is the initial primary ion activity and a'_A is the activity of A in the presence of interfering ion B. The results obtained are given in **Table 2**.

Interfering ions B	$K_{A,B}$ [MPM]
K^+	2.28×10^{-3}
Na^+	3.69×10^{-3}
Sr^{2+}	1.74×10^{-2}
Ni^{2+}	3.68×10^{-3}
Co^{2+}	9.00×10^{-3}
Cd^{2+}	1.60×10^{-2}
Fe^{2+}	1.17×10^{-3}
Mg^{2+}	3.98×10^{-2}
Cu^{2+}	3.68×10^{-3}
Zn^{2+}	5.97×10^{-3}
Pb^{2+}	5.03×10^{-3}
Be^{2+}	7.84×10^{-3}
Ca^{2+}	4.74×10^{-2}
Cr^{3+}	5.23×10^{-3}
Ce^{3+}	9.00×10^{-3}

Table 2 Selectivity coefficients of various interfering cations.

4. APPLICATIONS

The developed electrode was used as an indicator electrode in the titration of a 1.0×10^{-4} M Ba (II) solution with 1.0×10^{-2} M EDTA solution. The resulting titration curve is shown in **Figure 5**.

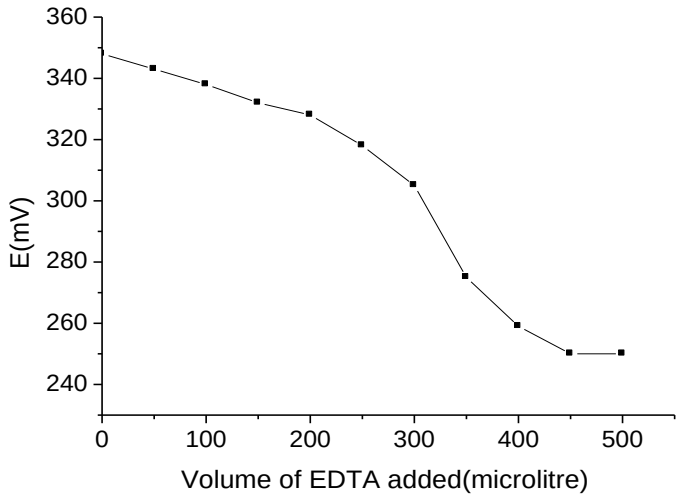

Figure 5 Titration of 30.0 cm^3 of 1.0×10^{-4} M Ba (II) with 1.0×10^{-2} M EDTA.

5. CONCLUSION

The developed graphite coated PVC-based membrane incorporating DB24C8 with composition 33.0% PVC, 57.0% o-NPOE, 6.0% NaTPB, 2.0% MWNT and 2.0% DB24C8 exhibited the best performance characterstics. The fabricated electrode illustrated a Nernstian response in the concentration range of 1.0×10^{-6} to 1.0×10^{-3} M, a detection limit of 6.1×10^{-7} M, and a fast response time of <10s in the pH range of 4.1 – 9.0.The fabricated membrane sensor revealed good selectivity for Ba(II) ions over a variety of other cations. The electrode was successfully used as an indicator electrode in the potentiometric determination of barium by titration with EDTA.

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