Full Paper

Trace Amounts Determination of Barium Ions by a New Ion-Selective Electrode based on 4′,4″(5″)-Di-Tert-Butyldibenzo-18-Crown-6

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Abstract- A poly(vinyl chloride) membrane sensor for barium was prepared using 4′,4″(5″)-Di-tert-butyldibenzo-18-crown-6 (DTB 18C6) as an ion carrier. The optimized membrane with PVC:DOP:DTB18C6:KTCPB percent ratio of 33:60:5:2 led to a Nernstian calibration slope of 25.23 mV per decade, from 1×10^{-7} to 1×10^{-1} M . Dioctyl phthalate was found to act as the best plasticizer in terms of controlling the response and durability of the sensor the lifetime of the fabricated sensor. The sensor had a short response time of 18 s and its response was independent from pH from 2.0 to 12.4 working pH ranges. The selectivity behavior of the sensor for barium in the presence of alkali, alkaline earth, transition and heavy metal ions was very good. The applicability of the sensor was evaluated through using it as an indicator in the potentiometric titration of SO_4^{2-} ions.

Keywords- Ion selective electrodes; PVC-membrane; Barium(II) ions; Potentiometric sensor

1. INTRODUCTION

Barium metal cannot be freely found in nature. It exists just from industrial emission. The inhalation of dust containing barium can lead to a range of diseases in human such asrhabdomyolosis, hypophosphatemia and baritosis [1,2]. Therefore, the measurement of compounds containing barium is necessary. Several analytical methods have been used for the barium ion monitoring, like atomic absorption spectroscopy (AAS) [3], ICP-AES [4], etc. The

techniques are too expensive and require more time for sample preparation, and hence developing alternative methods is desirable. During the past four decades, extensive research has been carried out on the development of ion-selective electrodes [5-7], which can be used to determine the activity of an ionic species by measuring the electrical potential of a solution. ISEs detect a specific ion among others in solution with fast response and simple construction [8-10]. PVC is widely used in the structure of membranes [11,12]. Some recent reports have described the development of barium-selective sensors [10,13-15].

Since Pedersen introduced crown ethers [16], more studies have focused on their properties and complexation reactions with metallic ions in solutions [17,18]. Several factors including the cavity size, nature of the donor atoms of the crown ring, functional groups, and solvents [19], influence the formation or stability of crown ether complexes with metallic ions in solution. Some crown ethers have been used as neutral ion carriers for constructing ion-selective electrodes [20-25]. In the present work, DTB18C6 (Figure 1) was used as an ionophore, in a PVC membrane further containing dioctyl phthalate (DOP) as a plasticizer, and an ionic additive (potassium tetrakis(*p*-chlorophenyl) borate (KTCPB)). The resulting liquid membrane barium selective electrode had a low limit of detection, short response time, and good selectivity for Ba^{2+} in the presence of various interfering ions.
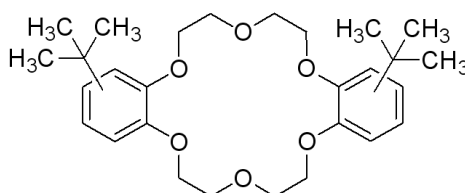

Figure 1. Chemical structure of DTB 18C6

2. EXPERIMENTAL SECTION

2.1. Chemicals

High relative molecular weight PVC, 4′,4″(5″)-Di-tert-butyldibenzo-18-crown-6, reagent grade Dioctyl phthalate (DOP), nitrophenyl octyl ether (NPOE), benzyl acetate (BA), sodium tetraphenylborate (NaTPB), and potassium tetrakis(*p*-chlorophenyl) borate (KTCPB), tetrahydrofuran (THF) were procured from Aldrich and used without any further treatments. All experiments were performed using triply distilled deionized water.

2.2. reparation of the membrane electrodes

In the case of the optimal sensor 5mg of the ionophore (DTB18C6), 33 mg of PVC powder, 60 mg of DOP, and 2 mg KTCPB were dissolved in 2mL of tetrahydrofuran. A similar procedure was used for preparing the rest of the membranes. Next, the mixture of the homogenized

ingredients was left in the air, so that to form an oily mixture, due to the evaporation of THF. Next, a 3 mm o.d. Pyrex tube [26-28] was inserted into the oily mixture and kept there for 10s to form a 0.3 mm membrane at its tip. The membrane was then left for 24 hours to dry at ambient conditions. In the next step, the tube was filled with 1.0×10^{-3} M Ba^{2+}, and an Ag-AgCl electrode was inserted into the solution to act as the internal reference.

2.3. Emf reading

The electromotive force (EMF) measurements using the membrane electrode as an indicator electrode was performed using a cell assembly as below:

Ag-AgCl | KCl (3M) | 1.0×10^{-3} M Ba^{2+} | PVC membrane | test solution | Ag-AgCl

The internal reference electrode was a double-junctions Ag-AgCl electrode with a 3 M potassium chloride solution.

3. RESULTS AND DISCUSSION
3.1. Initial Studies

First, the complexation reactions of DTB18C6 with Li^+, Na^+, K^+, Ba^{2+}, and Mg^{2+}, were studied in a non-aqueous media (acetonitrile) [17,18]. The results indicate the stability of the resulting complexes to vary as $Li^+ > Ba^{2+} > K^+ > Na^+ > Mg^{2+}$ [17]. Thus, in this research, we used the DTB18C6 as the Ba^{2+} ions selective ionophore.

3.2. Optimization of membrane composition

It has been established that the sensitivity profile and linearity of the response of an ion-selective electrode is not only a function of the properties of the ionophore but also depend on the nature and amount of the two other main ingredients namely the plasticizer and ionic additive [29-36].
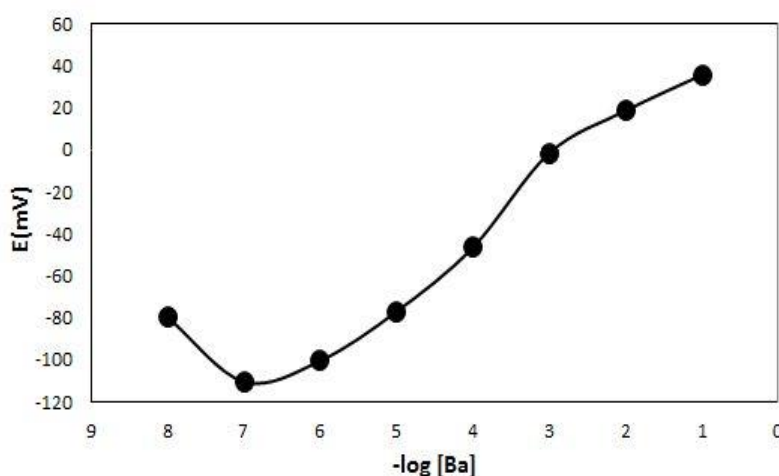

Figure 2. Calibration graph for the proposed PME electrode

Therefore, the effects of these factors on the potential response of the ion-selective electrode were studied, and the results are presented in Table 1. To record the data, various sensors were immersed 1×10^{-8} to 1×10^{-1} M barium ion solutions and the results corresponding to each composition were monitored and summarized in Table 1.

Table 1. Optimization of membrane ingredients

Membrane	Composition (٪)				Slope (mV/decade)
	PVC	Plasticizer	L	Additive	
1	32	BA,60	5	STPB,3	9.71
2	32	DOP,60	5	STPB,3	17
3	32	NPOE,60	5	STPB,3	11.5
4	32	DOP,60	5	STPB,3	11.65
5	33	DOP,60	4	STPB,3	12
6	31	DOP,60	6	STPB,3	8.68
7	33	DOP,60	5	STPB,2	21.17
8	31	DOP,60	5	STPB,4	17.42
9	32	DOP,60	5	KTCPB,3	22.4
10	33	DOP,60	5	KTCPB,2	25.23
11	31	DOP,60	5	KTCPB,4	16.04

Based on the observations membrane number 10 (33%wt. of PVC, 60%wt. of DOP, 5%wt. of DTB18C6, 2% wt. of KTCPB) revealed a Nernstian calibration plot with a slope of 25.23 mV/decade from 1.0×10^{-7} to 1.0×10^{-1} M (Figure 2). Table 2 summarizes the response characteristics of the developed ion-selective electrode.

Table 2. Response characteristics of the barium ion-selective electrode

Electrode	Slope (mV/decade)	Linear range (M)	LOD (M)	Response time (s)	Life time (week)
PME	25.23	1.0×10^{-7} - 1.0×10^{-1}	8.9×10^{-8}	18	10

3.3. Influence of the Internal Solution

The effect of the concentration of the internal solution on the response of the developed sensor was studied using three different solutions (i.e. 1.0×10^{-4}, 1.0×10^{-3} and 1.0×10^{-2} M) as the internal solutions and the emf-pBa curves were plotted (Figure 3). Based on the results, this had a negligible effect on the electrode response [37].
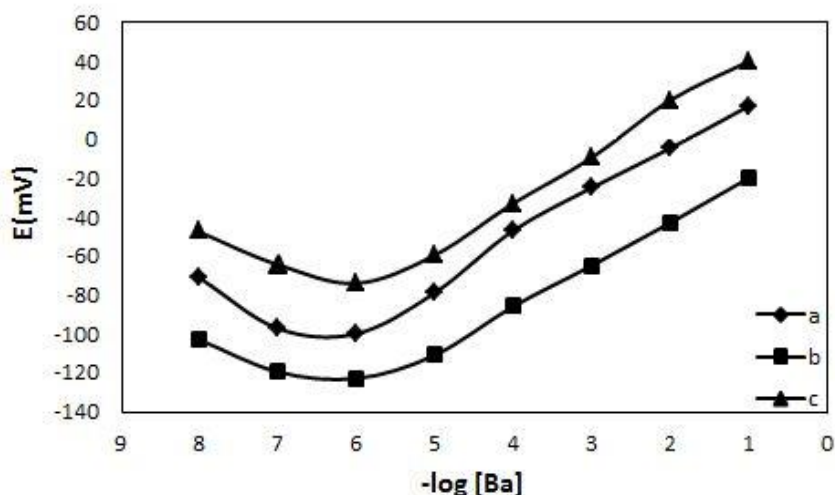
Figure 3. Effect of the internal solution. a: 10^{-2} M, b: 10^{-3} M, c: 10^{-4} M $Ba(NO_3)_2$

3.4. Effect of pH

The effect of changes in the pH of the test solution on the developed sensor was monitored by changing this factor from 1.0 to 14.0. The changes in the pH were created by adding small volumes of concentrated HCl or NaOH solutions to a 1.0×10^{-3} M Ba^{2+} solution, to avoid concentration change due to volume changes and the results of emf reading under these conditions are plotted in Figure 4. According to these results, the response of the sensor was independent of pH from 2.0 to 12.4. The significant changes in the electrode response at higher pH values are caused by the formation of soluble hydroxy complexes of Ba^{2+} ion, while this behavior at lower pH values corresponds to the protonation of the donor atoms of the ligand, and in other words, the response of the sensor to H^+ [33-37].
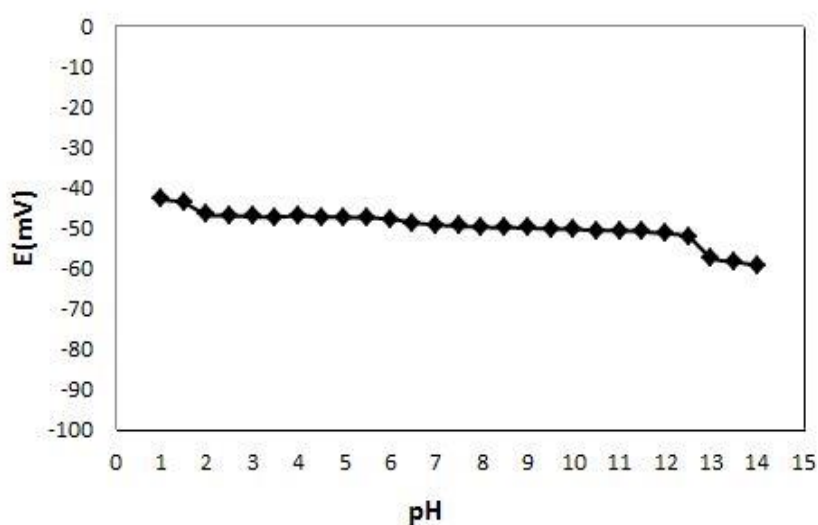

Figure 4. Influences of pH of the test solution on the potential response of the PME in the presence of 1.0×10^{-3} M Ba^{2+}

3.5. Response time of the sensor

The dynamic response time of a sensor is a factor in evaluating the sensor [38-41]. This factor was determined by measuring the average time the sensor requires to reach a potential value within ± 1 mV of its equilibrium potential after a tenfold concentration change in the test solution, created through successive immersions of the sensor into a set of Ba^{2+} solutions. The response time of the developed sensor was determined to be below 20 s (Figure 5).
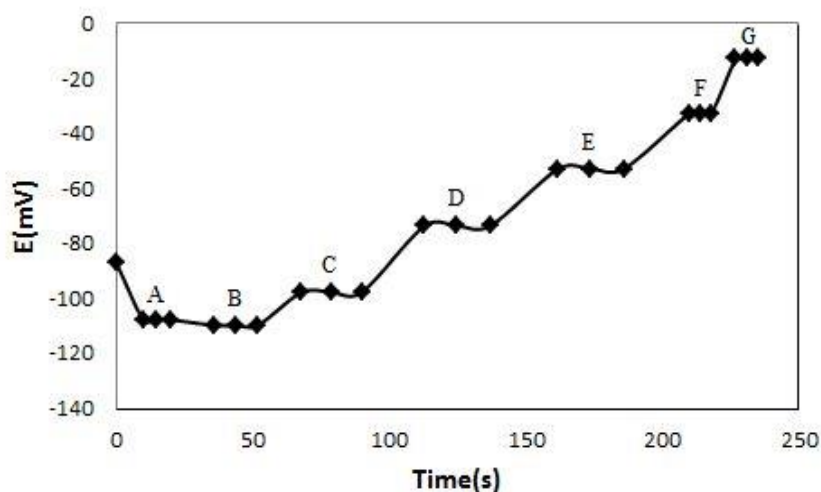

Figure 5. Typical dynamic response of the proposed electrode for step change concentrations from low to high: A) 1.0×10^{-7}, B) 1.0×10^{-6}, C) 1.0×10^{-5}, D) 1.0×10^{-4}, E) 1.0×10^{-3}, F) 1.0×10^{-2}, G) 1.0×10^{-1} M Ba^{2+}

3.6. Selectivity Coefficients

The effect of the presence of interfering ions on the potential response of the Ba^{2+} electrode can be presented as a selectivity coefficient ($K_{Ba,M}^{pot}$) [42]. which reflects the preference of the sensor to an interfering ion M^{n+} as opposed to Ba^{2+}. In this study, the separated solutions method was used [43].

Table 3. Selectivity coefficient of various interfering ions

Interfering ion	Selectivity coefficient
Ca^{2+}	1.7×10^{-2}
Zn^{2+}	2.3×10^{-2}
Al^{3+}	1.71×10^{-3}
Fe^{3+}	5.7×10^{-3}
K^+	$2 \times 10^{4+}$
Ag^+	$2 \times 10^{2+}$
Na^+	$2.5 \times 10^{3+}$
Hg^{2+}	1.1

To do this first the emf-pM^{n+} plots of independent solutions of barium and various interfering ions were obtained using the sensor. Next, the selectivity coefficient was determined using a pair of primary (a_A) and interfering (a_B) ion concentrations where the electrode produces an identical potential in separate solutions (i.e., isopotential concentrations) and equation $K_{A,B}^{pot} = \ln a_A / a_B^{2/z}$ (z being the charge of interfering ion) [37] (Table 3). The observations indicated that the sensor has a high selectivity for Ba^{2+} as in comparison to Ca^{2+}, Zn^{2+}, Al^{3+} and Fe^{3+} but K$^+$, Ag$^+$, Na$^+$ and Hg^{2+} (Figure 6).
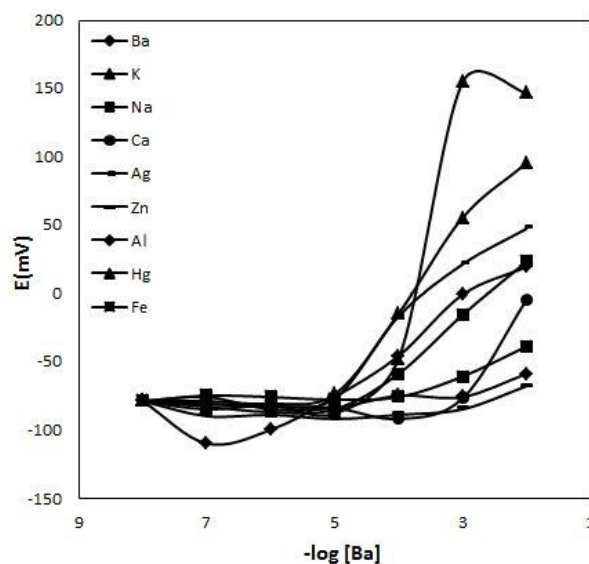

Figure 6. Selectivity coefficient of various interfering ions

3.7. Analytical applications

3.7.1. Comparison with other reported methods

The results obtained from the developed sensor were compared with those of other barium-selective electrodes (Table 4). As shown in Table 4 data, the present sensor offers a better detection limit (5.0×10^{-7} M), a wide applicable pH window of 2.0-12.4 and a faster response.

Table 4. The performance characteristics of Ba-DTB18C6 membrane sensor compared with other barium sensors

Parameter	Reported sensors						Present work
	[11]	[45]	[44]	[2]	[13]	[14]	
Slope (mV/decade)	32.5	26.6	30	30	28.5	29.7	25.23
LLLR^a(M)	-	1×10^{-5}	-	1.4×10^{-6}	1×10^{-5}	3.6×10^{-6}	-
LLD^b(M)	1.0×10^{-6}	3×10^{-6}	3.0×10^{-6}	-	2.5×10^{-6}	1.9×10^{-6}	8.9×10^{-8}
pH range	2-8	2-10	6-8	2.5-7	4.5-10	2.5-7.5	2.0-12.4

^{a} LLLR(M): Lower limit of linear range
^{b} LLD(M): Lower limit of detection

3.7.2. Analysis of Ba^{2+} in wastewater

A wastewater sample was applied for the analysis of Ba^{2+} by the standard addition method. The wastewater sample has various materials such as Ba^{2+}, Cu^{2+}, Fe^{3+} and Zn^{2+} and was analyzed by the reported analysis method [13]. The results are given in Table 5.

Table 5. Analysis of barium(II) ions in wastewater

Sample	Barium found (M)	
	ISE	AAS
1	2.83×10^{-4}	2.91×10^{-4}

3.7.3. Sulfate (II) ion concentration in potable water

The proposed membrane electrodes were successfully used as an indicator in the potentiometric titration of a 1.0×10^{-3} M Ba^{2+} solution using a 1.0×10^{-3} M solution of sulfate ion and the resulting plot is given in Figure 7.
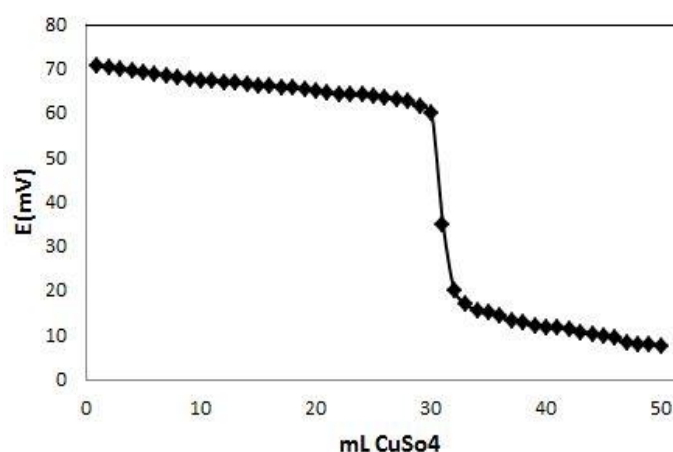

Figure 7. Potentiometric titration curve of 30.0 mL 1.0×10^{-3} M of Ba^{2+} with 1.0×10^{-3} M solution of copper sulfate

4. CONCLUSION

Using 4′,4″(5″)-Di-tert-butyldibenzo-18-crown-6 as a selective ion carrier for Ba^{2+} led to positive results in terms of sensitivity and selectivity. The sensor based on dioctyl phthalate as a solvent mediator produced the best results in terms of a response slope of (25.23 mV per decade), and applicability range (1×10^{-7} to 1×10^{-1} M), while ortho nitrophenyl octyl ether and benzyl acetate did not produce acceptable results. The good selectivity of the sensor could be attributed to the favorable size of the cavity of the ionophore, as well as the presence of 6 hard

donating oxygen atoms in its structure which gave the ionophore the potentials for strong interactions with the target ion. The maximum interference was observed for Zn^{2+} and Ag^+ ions with selectivity coefficients of 2.3×10^{-2} and 2.3×10^{-2} which are acceptable values to guarantee the accuracy of the sensor response in the presence of moderate concentrations of interfering ions. The other factors including the response time, applicable pH range and the applicability of the sensor in the analysis of barium concentration, prove the developed sensor as a robust portable tool for the analysis of Ba^{2+}, with advantages over the existing ion selective electrodes for this ion in terms of the detection limit and applicable pH range.

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