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ORIGINAL ARTICLE

Polymeric membrane coated graphite cesium selective electrode based on 4′,4″(5′) di-tert-butyldibenzo-18-crown-6

Susan Sadeghi · Fatemeh Fathi

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Abstract A new PVC membrane coated graphite electrode for cesium ion based on 4′,4″(5′)di-tert-butyldibenzo-18-crown-6 (DTBDB18C6) as ionophore was prepared. The electrode shows a near Nernstian response of 57.0 ± 1.8 mV decade^{-1} over a wide activity range of 6.0×10^{-6} –1.0×10^{-1} mol L^{-1} with a limit of detection 4.0×10^{-6} mol L^{-1}. The proposed electrode is suitable for use in aqueous solution in the pH range of 3.0–9.5. It has a fast response time of 10 s and can be used for at least 1 month without any considerable divergence in potential. The selectivity coefficients for Cs^+ ion with respect to ammonium, alkali, alkaline earth and some selected transition metal ions were determined and showed a superior selectivity over Li^+, Na^+ and alkaline earth metal ions. The new electrode was applied for determination of Cs^+ in spiked tap water. The electrode was also used as indicator electrode in potentiometric titration of Cs^+ with sodium tetraphenyl borate.

Keywords Cesium · Coated graphite membrane electrode · Potentiometric determination · 4′,4″(5′)Di-tert-butyldibenzo-18-crown-6

Introduction

The ion selective electrodes (ISEs) based on polymeric membranes incorporated with ionophores are well known as very useful tools for clinical, chemical and environmental analysis. Up to now, many ionophores with high selectivity to metal ions have been developed for the potentiometric determination of the respective metal ions. Potentiometric determination of analyte using ISE is considered as a quick, simple and inexpensive method of analysis in comparison with other analytical methods such as atomic absorption or inductively coupled plasma spectroscopy. Determination of heat generating nuclides and long-life nuclides such as cesium and strontium ions is of particular interest. Cesium selective electrodes are useful analytical tools for determination of radioactive Cs^+ isotopes in nuclear waste water because no chemical methods are available for in situ cesium analysis in these solutions [1, 2]. A great deal of efforts has gone toward finding selective ionophores toward cesium ions. The compounds which have high Cs^+/Na^+ selectivity are special need for sensing Cs^+ in radioactive waste waters. Several types of ionophores have been reported including antibiotic cephalexin [3], Calixaren [4–9], Cs-12-molybdophosphate [10], crown ethers [11–16], crown formazans [13, 17], aniline derivatives [18], pyron compounds [19], polymeric microspheres [20] and Zeolite [21]. Crown ethers have been employed as ionophore in Cs^+-ISE. The feature of crown ethers gives geometric and cavity control of host–guest complexation and its lipophilicity might produce remarkable selectivity and stability for a specific ion. Calix [4] arene crown-6 derivatives was reported as selective ionophore toward Cs^+ over Na^+ [22]. According to the literature [23], attachment of phenyl rings to 18-crown-6 markedly improved selectivity of the ionophore to alkali ions due to the additional π-interactions between the cation locating in the crown ring cavity and neighboring two parallel aromatic nuclei. In this work, we interested to investigate the influence of tert-butyl groups attached to benzene rings in DTBDB18C6 on complexation of Cs^+ and potentiometric response of the ionophore incorporated in solvent polymeric membrane electrodes. Due to extremely simple,

S. Sadeghi (✉) · F. Fathi
Department of Chemistry, Faculty of Science, Birjand University, Birjand, Iran
e-mail: ssadeghi@birjand.ac.ir; chemsad2001@yahoo.com

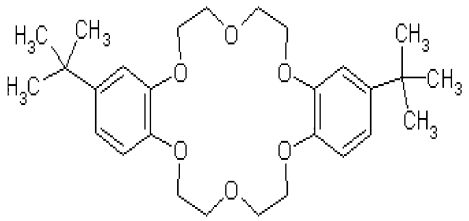

Fig. 1 The chemical structure of the DTBDB18C6

inexpensive and easy preparation as well as possibility of elimination of the internal filling solution and the stability of potentials in coated graphite electrode (CGE), we report on the fabrication of new coated graphite liquid membrane electrode based on DTBDB18C6 (Fig. 1) for determination of Cs^+ ions. The proposed electrode exhibited fast response time and high selectivity towards Cs^+ ions.

Experimental

Reagents and materials

Reagent grade 2-nitrophenyl octyl ether (*o*-NOPE), sebacic acid dibutyl ester (DBS), dibutyl phthalate (DBP), dioctyl phthalate (DOP), sodium tetra phenyl borate (NaTPB), potassium tetrakis (*p*-chlorophenyl) borate (KT*p*ClPB), 4′,4″(5′)di-tert-butyldibenzo-18-crown-6 (DTBDB18C6) and high molecular weight poly (vinyl chloride) (PVC) were of selectophore and obtained from Fluka. Benzyl acetate (BA), oleic acid (OA) and tetrahydrofuran (THF) were of extra pure grade and purchased from Merck. Cesium nitrate and nitrate or chloride salts of all other cations with highest purity available were obtained from Merck. All standard solutions were freshly prepared with deionized doubly distilled water.

Preparation of polymeric ion-selective electrode

Prior to use, the graphite electrodes were cleaned with concentrated HNO_3, THF and doubly distilled water and then dried at 100 °C. A typical membrane consists of 8.0 wt% ionophore, 1 wt% NaTPB, 58 wt% DOP and 33 wt% PVC. All the components were dissolved in 2 mL of THF. The CGEs were produced by dipping 5 mm of a polished graphite rod (3 mm diameter and 10 mm length) directly into the membrane solution for 30 s to form a transparent membrane at the end of rod. The graphite rod was then pulled out from the solution and kept for one day to allow the solvent to evaporate at room temperature. The compositions of all membranes used in this study are listed in Table 1. The electrodes were finally conditioned by soaking in a 1×10^{-4} mol L^{-1} $CsNO_3$ solution for 24 h.

Potentiometric measurements

The potential differences between the cesium-CGE and the double junction calomel electrode were measured using a digital mV meter WTW (Weilheim, Germany) at room temperature by setting up the following cell assembly:

Graphite electrode | PVC membrane | test solution | 0.1 M KCl | Hg_2Cl_2 | Hg

All emf measurements were conducted in unstirred solutions. Activity coefficients of ions in aqueous solutions were calculated according to the modified Debye-Hückle equation [24]. At least, three time measurements were performed for each solution.

Results and discussion

By considering of the cavity diameter of dibenzo-18-crown-6 (2.6–3.4 Å) and the ionic diameters of the alkali metal cations (1.36–3.3 Å), it is anticipated that some cations such as Rb^+ and Cs^+ are too large to be accommodated in the cavity of the polyether and should form sandwich-type complexes at 1:2 ratio of metal: polyether. It is also proved that attachment of even the smallest alkyl group (i.e., methyl) at the geminal position of benzo-16-crown-5 induced a marked enhancement in the Na^+/K^+ selectivity. The effect of functional tertiary-butyl group on the phenyl ring attached to the crown ether as the ionophore used in this work on cation response order would thus be important to study. Thus, in a preliminary experiment, DTBDB18C6 was used as ionophore to prepare the plasticized PVC membranes for a wide variety of cations. The potential responses of the CGEs based on DTBDB18C6 were examined in the activity range of 1.0×10^{-7}–1.0×10^{-1} mol L^{-1} solutions containing a single type of cation. The alkali and alkaline earth metal ions calibration plots of the CGE based on DTBDB18C6 are shown in Fig. 2. It was found that among different cations tested, except for the Cs^+, the plot of potential versus log a_{cation} showed less steep slopes than the expected for mono or divalent cations.

The potentiometric ion selectivity of solvent polymeric membrane electrodes depends on the composition of the ion-selective membranes that can be optimize experimentally. Optimization of the PVC membranes containing DTBDB18C6 was studied on the basis of the Log $K^{pot}_{Cs,M}$ values, linear range, slope and detection limit for Cs^+ ion. At first, Log $K^{pot}_{Cs,M}$ values were evaluated for most interfering ions K^+, Rb^+ and NH_4^+ ions since their size is close that of cesium. The results are summarized in Table 1.

The plasticizer or membrane solvent greatly affects all the electrochemical characteristics including potentiometric selectivity. The dielectric constant, ε, of the PVC membrane is a function of nature of the plasticizer as well

Table 1 Composition and potentiometric characteristics of Cs^+-selective membranes based on DTBDB18C6

Membrane no.	Ionophore[a] (%)	PVC (%)	Composition						Activity linear range (mol L^{-1})	LOD (mol L^{-1})	Slope (mV decade^{-1})	Log K^{pot}
			Plasticizer (%)					Additive (%)				
			DOP	*o*-NPOE	DBP	DBS	BA					Rb^+, K^+, Na^+, NH_4^+
1	5	33	62					–	1.0×10^{-5}–1.0×10^{-1}	6.0×10^{-5}	48.0 ± 0.2	−0.3, −0.5, −0.6, −0.9
2	5	33		62				–	1.0×10^{-4}–1.0×10^{-2}	1.0×10^{-5}	44.0 ± 0.7	–
3	5	33			62			–	1.0×10^{-5}–1.0×10^{-1}	1.0×10^{-5}	39.7 ± 3.0	–
4	5	33				62		–	1.0×10^{-4}–1.0×10^{-1}	9.0×10^{-5}	25.0 ± 3.8	–
5	5	33					62	–	–	–	1.5 ± 0.4	–
6	0	33	67					–	1.0×10^{-3}–3.2×10^{-2}	3.2×10^{-4}	10.8 ± 2.0	–
7	1 (137.0)	33	65					NaTPB, 1	1.0×10^{-5}–1.0×10^{-1}	1.0×10^{-5}	40.0 ± 0.8	−0.2, −0.3, −0.7, −0.9
8	3 (45.0)	33	63					NaTPB, 1	1.0×10^{-5}–1.0×10^{-1}	1.0×10^{-5}	47.6 ± 1.3	−0.3, −0.3, −0.5, −1.0
9	5 (27.5)	33	61					NaTPB, 1	1.0×10^{-5}–1.0×10^{-1}	1.0×10^{-5}	51.0 ± 0.8	−0.5, −0.3, −0.7, −0.9
10	8 (17.0)	33	58					NaTPB, 1	6.0×10^{-6}–1.0×10^{-1}	4.0×10^{-6}	57.0 ± 1.8	−0.9, −0.7, −1.8, −1.7
11	11 (12.5)	33	54					NaTPB, 1	1.0×10^{-5}–1.0×10^{-1}	1.0×10^{-5}	51.0 ± 0.8	−0.4, −0.4, −1.2, −1.5
12	8 (11.8)	33	58					KTpClTPB, 1	1.0×10^{-4}–1.0×10^{-1}	1.0×10^{-4}	49.6 ± 1.5	−0.3, −0.2, −0.4, −0.8
13	8 (21.0)	33	58					OA, 1	1.0×10^{-5}–1.0×10^{-1}	1.0×10^{-5}	52.0 ± 2.0	−0.3, −0.5, −0.5, −0.9

[a] Values in the parentheses are the additive to ionophore molar ratio

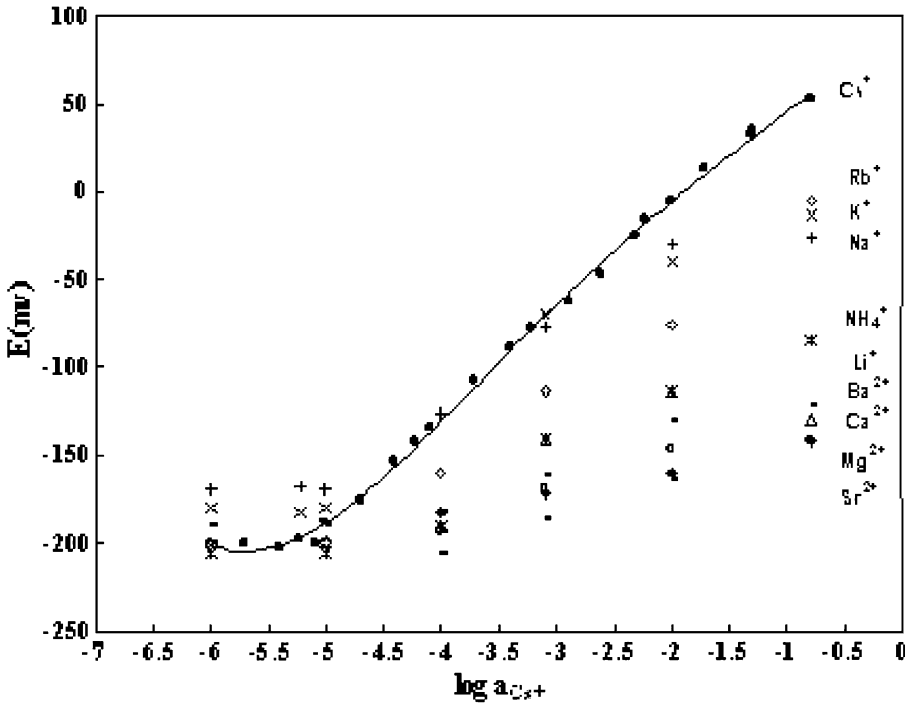

Fig. 2 Potentiometric response of various CGEs based on DTBDB18C6 with composition of the membrane No. 1

as its properties in polymeric matrix. Because the ISE contains 60–70% by weight of a plasticizer, the dielectric constant, ε, of the liquid membrane is similar to that of the pure liquid plasticizer. First, plasticized PVC membranes with the same ionophore content which differed in the polarity of the plasticizers, i.e. DBS ($\varepsilon = 4.54$), DOP ($\varepsilon = 5.1$), BA ($\varepsilon = 5.0$), DBP ($\varepsilon = 6.4$) and *o*-NPOE ($\varepsilon = 23.9$) were prepared. The results in Table 1 show that the membranes were made with DOP have wider linear dynamic range and slope than those of *o*-NPOE. Although the polar plasticizer may be attributed to lowering of the membrane resistance but the lipophilicity of plasticizer influences both the dielectric constant of the membrane and the membrane mobility of the ionophore [25].

Besides the critical role of the nature of plasticizer, the interaction between the ionophore and Cs^+ ions is also important for the membrane response, as blank membranes without ionophore have shown a slope of only 10.8 mV/decade and the detection limit of 3.2×10^{-4} M. Therefore, dependence of response of the electrodes on the amount of ionophore in the membrane composition was examined. As Table 1 shows, with increase of the amount of ionophore from 1 to 8 wt% in the membrane, the slope of the electrode increases from 40.0 to 57.0 mV decade^{-1} and the detection limit improves from 1.0×10^{-5} to 4.0×10^{-6} mol L^{-1}, respectively. The selectivity coefficients also depend on the concentration of the cation–ionophore complex in the PVC membrane and extraction equilibrium at the interface between the membrane and aqueous solution, so as the amount of ionophore is increased, the membrane selectivity to Cs^+ over K^+ and Rb^+ is enhanced. Any increase in the ionophore content in the PVC membrane above 8 wt% resulted in diminished sensitivity of the membrane most probably due to inhomogeneous distribution of the ionophore in the film and possible saturation of the membrane.

It is well known that the incorporation of a certain ratio of fixed anionic sites into the membranes improves selectivity of cation selective electrodes [26, 27]. Thus, various DTBDB18C6 based membranes with the same ionophore and DOP plasticizer but different anionic sites, i.e. NaTPB, KT*p*ClPB or OA were prepared and the potentiometric responses of the electrodes were tested. As can bee seen from Table 1, the membrane in the presence of NaTPB showed an improved slope compared with the membranes without NaTPB. The membranes with OA or KT*p*ClTPB gave the narrow working concentration range and decreased slope of the electrode. The relevant selectivity coefficients showed that the Cs^+ selectivity of the membrane system was increased with the increase of the molar percentage of NaTPB to ionophore up to 17%. The best performance was exhibited by membrane No. 10 with the composition of DOP:DTBDB18C6:NaTPB:PVC in the weight ratio of 58:8:1:33.

The calibration curve of the electrode based on the DTBDB18C6 display a linear activity range of 1.0×10^{-1} to 6.0×10^{-6} mol L^{-1} and a slope of 57.0 ± 1.8 mV

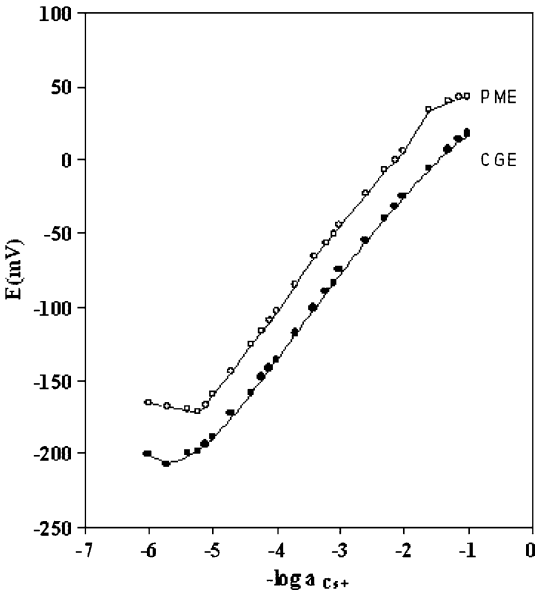

Fig. 3 Calibration curves of the PME and CGE based on DTBDB18C6 toward Cs^+ ion with composition of the membrane No. 10

decade^{-1} to Cs^+ ion. The limit of detection which was estimated at the intersection of two extrapolated segments of the calibration graph found to be 4.0×10^{-6} mol L^{-1}. For comparison, the classical membrane electrodes with the same composition of the membrane No. 10 were prepared and the potentiometric characteristics of these electrodes were studied. The EMF response of the classical polymeric membrane (PME) and coated graphite electrode (CGE) to Cs^+ ions are illustrated in Fig. 3. The slope, linear activity range and detection limit of the resulting EMF-pCs^+ graph for PME are 57 mV decade^{-1}, 7.5×10^{-6}–2.5×10^{-2} mol L^{-1} and 7.5×10^{-6} mol L^{-1}, respectively. While both electrodes show a near Nernstian behavior with fast response time, the linear range and the limit of detection of the CGE are significantly improved relative to those of polymeric membrane electrode. The improved performance characteristics of the CGE over those of the PME presumably originate from the coated graphite technology, where an internal 1.0×10^{-4} mol L^{-1} $CsNO_3$ solution, in the case of PME, has been replaced by a copper wire of much higher electrical conductivity, in the case of CGE and lack of the leakage of the internal solution into the test solution via polymeric membrane.

The influence of pH on the potentiometric response of the electrode was examined in two fixed concentrations of Cs^+ (1.0×10^{-4} and 1.0×10^{-3} mol L^{-1}) at pH range of 2.0–12.0. The pH of solution was adjusted with either hydrochloric acid or sodium hydroxide solutions. As it is seen from Fig. 4, the potential response remains unaffected by change in the pH range of 3.0–9.5. However, beyond pH 9.5, the electrode response changes considerably. The

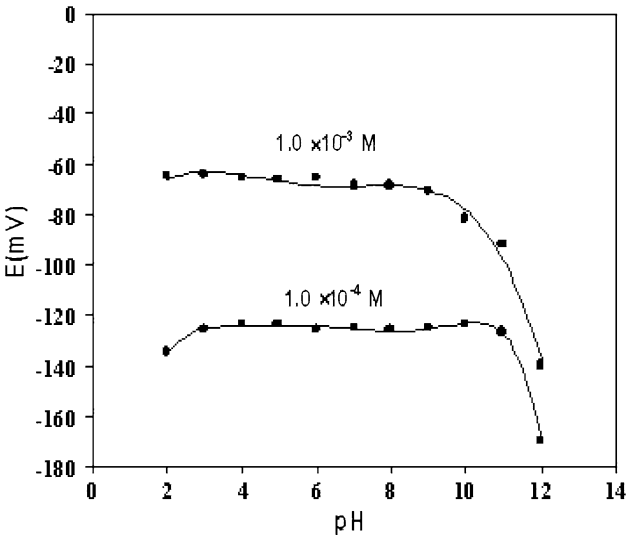

Fig. 4 pH response of the proposed electrode in 1.0×10^{-3} and 1.0×10^{-4} mol L^{-1} $CsNO_3$

observed drift at higher pH values could be due to contribution of Na^+ ions in solution resulting in a loss of the ability to complex with Cs^+, while the potential variations at below pH 3.0 indicating that Donnan failure took place by the chloride anions formed by hydrochloric acid. Therefore, pH range of 3.0–9.5 may be taken as the working pH range of the proposed electrode.

Dynamic response time is an important factor for any ion-selective electrode. In this study, the practical response time was recorded by changing the Cs^+ concentration in solution, over a concentration range 1.0×10^{-5}–1.0×10^{-2} mol L^{-1}, and the potential measurements were recorded every 5 s at room temperature. As can be seen from Fig. 5, the electrode reaches the equilibrium response

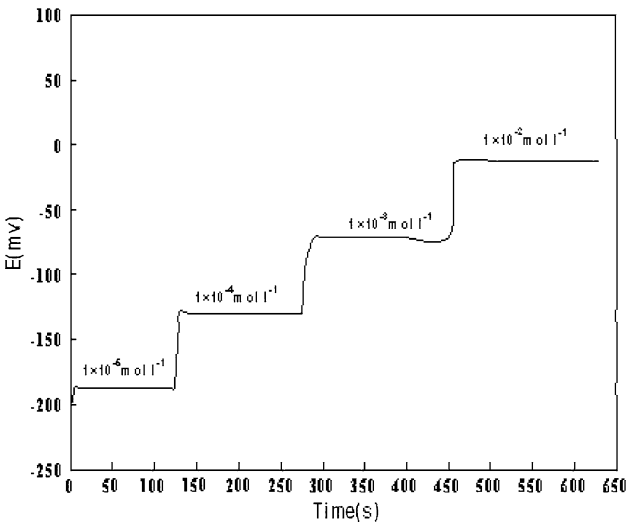

Fig. 5 Dynamic response time of the CGE based on DTBDB18C6 for step changes in concentration of Cs^+ ion from 1.0×10^{-5} to 1.0×10^{-2} mol L^{-1}

Table 2 Potentiometric selectivity coefficient values of various interfering cations using CGE based on DTBDB18C6

M^{n+}	Log $K^{pot}_{Cs,M}$	M^{n+}	Log $K^{pot}_{Cs,M}$
NH_4^+	−1.67	Ba^{2+}	−4.01
Na^+	−1.80	Pb^{2+}	−2.52
K^+	−0.70	Zn^{2+}	−3.81
Rb^+	−0.87	Sr^{2+}	−3.80
Li^+	−3.70	Cd^{2+}	−3.38
Mg^{2+}	−4.01	Cu^{2+}	−3.98
Ca^{2+}	−4.45	Ni^{2+}	−3.12
Co^{2+}	−3.00		

in a short time less than 10 s. This fast potentiometric response is most probably due to fast exchange kinetic of complexation–decomplexation of Cs^+ ion with the ionophore in surface layer at the test solution-membrane interface.

The stability of the membrane in both slope of the calibration curve and the detection limit was checked. After 1 month, the electrochemical behavior of the electrode gradually decreased with a ±2 mV divergence in slope.

The selectivity coefficient of the electrode is very important for evaluation of quality of the electrode to determine the target ion in the presence of the other ions. The selectivity coefficients of CGE with respect to interfering ions were evaluated with the separate solutions method (SSM) [28] and the results are summarized in Table 2. A general trend, that the selectivity toward an ion decreases with a decrease of ion size for both alkali and alkaline earth metal ions, is shown. For NH_4^+, hydrogen bonding to the polyether oxygen of the crown ether ring may also be an important factor in its complexation. Heavy metal ions have low values of Log $K^{pot}_{Cs,M}$ (−3 to −4) and therefore normally these would not cause any interference when present in the test solution at high concentration of 1.0×10^{-2} mol L^{-1}. For comparison, coated graphite electrodes based on dibenzo-18-crown-6 (DB18C6) as ionophore with the membrane composition No. 10 were prepared and potentiometric characteristics of the electrodes toward Cs^+ ions were investigated (Table 3). The results show that the presence of two tertiary-butyl groups make the dibenzo-18-crown-6 structure less flexible to reduce the approach of other ions, thus, it discriminates ions better than dibenzo-18-crown-6 ionophore. Kim et al. has reported this effect for Thiacalix [4] crown [29]. The comparison of the response characteristics of the electrode based on DTBDB18C6 with some previously reported for Cs^+-selective electrodes [8, 10, 12, 13, 17–19, 30, 31] are shown in Table 3. This comparison suggests that the proposed electrode is superior or comparable to those previously reported for Cs^+ ion with respect to the selectivity coefficients, response time and detection limit.

Application

To evaluate the analytical application of the proposed CGE, it was used as an indicator electrode in titration of 25 mL Cs^+ solution (1.0×10^{-3} mol L^{-1}) with NaTPB (1.0×10^{-2} mol L^{-1}) to determine the end point in the potentiometric titration. The change of potential was recorded after each addition of 0.1 mL of NaTPB solution

Table 3 Comparison of the analytical performance of Cs^+ selective CGE based on DTBDB18C6 with several recent works

Ionophore	Linearity (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mV decade^{-1})	Log $K^{pot}_{Cs,J}$				
				Li^+	Na^+	K^+	Rb^+	NH_4^+
Anilino-(1,3-dioxo-2-indanylidene)acetonitrile [18]	$0.1–2.5 \times 10^{-5}$	6.3×10^{-6}	52.0	−3.33	−2.72	−1.22	−0.70	−1.59
15-Crown-5 phosphotungustic acid precipitate [30]	$0.1–1.0 \times 10^{-4}$	1.0×10^{-5}	60.0	−0.89	−0.46	−0.31	−0.46	–
14,15-Crown-formazans [13]	$0.1–5.0 \times 10^{-4}$	2.0×10^{-4}	50.0	−2.5	−2.85	−1.46	–	−1.39
3,5-Bis[(2-formyl phenoxy)-methyl]-2,6-diphenyl-4H-pyran-4-one [19]	$0.1–3.0 \times 10^{-5}$	3.0×10^{-5}	57.7	−1.40	−1.15	−1.30	−0.57	−1.30
2,3Benzoquino(15)crown-5 [31]	$0.1–1.0 \times 10^{-4}$	5.0×10^{-5}	51.9	−3.00	−2.38	−0.99	−0.47	−1.40
Cs-12-molybdophosphate [10]	$0.1–1.0 \times 10^{-5}$	3.0×10^{-6}	46.5	–	−0.62	−0.62	–	−1.00
Calix[4]biscrown-6 [8]	2.0×10^{-3} $–1.0 \times 10^{-6}$	1.0×10^{-6}	57.5	–	−4.9	−2.5	−0.7	–
Bis(benzo-18-crown-6) [12]	7.9×10^{-2} $–5.0 \times 10^{-5}$	1.0×10^{-5}	57.0	–	−2.0	−1.0	−1.9	−1.7
This work (CGE)	$0.1–6.0 \times 10^{-6}$	4.0×10^{-6}	57.0	−3.70	−1.80	−0.70	−0.87	−1.67
This work (CGE)	$0.1–1.0 \times 10^{-4}$	8.7×10^{-5}	49.0	–	−1.17	−0.13	−0.15	−1.10

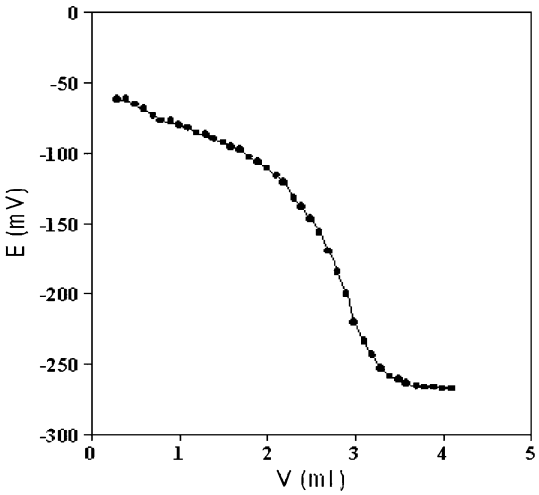

Fig. 6 Potentiometric titration curve for 25 mL of 1.0×10^{-3} mol L^{-1} Cs^+ solution with 0.01 mol L^{-1} NaTPB using the proposed electrode as indicator electrode

Table 4 Results of the Cs^+ recovery from the spiked tap water by the proposed electrode (n = 3)

No.	Added	Concentration of Cs^+ ion (μg mL^{-1})	
		Found by AAS	Found by Cs^+ ISE
1	6	6.05 ± 0.10	6.25 ± 0.20
2	12	12.06 ± 0.10	12.10 ± 0.16

(Fig. 6). The resulting titration curve showed a linear potential drop with an inflection point at 2.5 mL of the titrant indicating the amount of Cs^+ can be accurately determined with the electrode. The practical utility of the proposed electrode was also investigated by potentiometric determination of the Cs^+ concentration in tap water spiked with 6 and 12 μg mL^{-1} Cs^+. The standard addition method was used for the determinations. Good agreement of the results obtained using the proposed electrode with those obtained by atomic absorption spectrometry (AAS) (Table 4) could make this procedure a relatively reliable method.

Conclusion

The prepared coated graphite rod Cs^+-ISE (CGE) incorporating DTBDB18C6 as a sensing material could be used to determine cesium ion over the activity range of 6.0×10^{-6}–1.0×10^{-1} mol L^{-1} with a slope of 57 mV/decade at the pH range of 3.0–9.5. The short response time of the electrode suggests it can be applied for cesium determination in dynamic conditions. The electrode exhibited good performance characteristics such as detection limit and selectivity coefficients.

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