

Potassium-Selective Membrane Sensors Based on Two Recently Synthesized Poly(oxyethylene) Derivatives[☆]

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ABSTRACT: Two poly(oxyethylene) derivatives 1,10-bis(2'-benzoic acid)-1,4,7,10-tetradecane (L1) and 1,7-bis(2'-benzoic acid)-1,4,7-trioxaheptane (L2) were used as suitable ionophores for the preparation of potassium-selective PVC-membrane electrodes. The resulting electrodes based on L1 and L2 exhibit linear responses to the activity of K^+ ions within the concentration ranges of 3.1×10^{-5} - 2.7×10^{-2} M and 2.0×10^{-5} - 7.3×10^{-2} M with the slopes of 61.8 and 62.6 mV per decade, respectively. The electrodes show relatively fast response times of 25-30 s and can be used for at least 3 months without any considerable divergence in potential. The working pH range of the electrodes is 3-11. The selectivity coefficients of the electrodes for potential interfering cations including alkali, alkaline earth and transition metal ions are reported.

KEY WORDS: K^+ ion-selective electrodes, PVC membrane, Poly(oxyethylene), Potentiometry.

INTRODUCTION

Potentiometric ion-selective membrane electrodes for K^+ ion are steadily replacing flame photometry and other analytical techniques for monitoring potassium ion in various matrices [1,2]. These membrane sensors incorporate antibiotics such as valinomycin [3-6], crown ethers [7-9], bis-crown ethers [10-12] and other macrocyclic ligands [13-15]. The nature and characteristics of various types of potassium ion-selective electrodes have been reviewed [16]. Although valinomycin is, by far, the most successful ionophore for construction of K^+ -selective

sensors, it suffers some essential drawbacks. Valinomycin is a very expensive reagent with potentiometric selectivity in the order $Rb^+ > Cs^+ > K^+ \gg Na^+$ [6]. Moreover, it possesses relatively low lipophilicity which results in decreased lifetime of the membrane sensors.

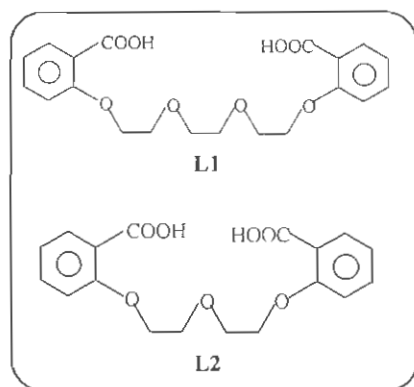
On the other hand, in comparison with extensive use of macrocyclic compounds, the use of noncyclic ligands in construction of potassium ion-selective electrodes is quite sparse. Saleh et al. have reported the use of some alkylthiophosphate compounds [17] and phosphine oxide

[☆] Dedicated to Professor Mahdi Golabi on the occasion of his 67th birthday.

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derivatives [18] as neutral acyclic ionophores in preparation of potassium selective sensors. In this paper we report the successful use of two lipophilic poly(oxyethylene) derivatives 1, 10-bis(2'-benzoic acid)-1,4,7-tetraoxadecane (L1) and 1,7-bis(2'-benzoic acid)-1,4,7-trioxaheptane (L2) [19] as suitable ionophores in preparation of new K^+ ion-selective electrodes. The poly(oxyethylene) derivatives are well known to form stable and selective complexes with alkali metal cations of proper size [20,21].



EXPERIMENTAL

Reagents

Reagent grade dibutyl phthalate (DBP), high relative molecular weight PVC, tetrahydrofuran (THF) and sodium tetraphenylborate (NaTPB) were purchased from Fluka chemical company and used as received. The chloride and nitrate salts of all cations used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5 . The ionophores L1 and L2 were synthesized and purified as described elsewhere [19]. Triply distilled deionized water was used throughout.

Electrode preparation

The general procedure to prepare the membranes was to mix the optimized ingredients thoroughly (i.e., 65.6 mg of DBP, 26.5 mg of PVC, 7.2 mg of L1 and 0.7 mg of NaTPB, in the case of L1 membrane, and 67.1 mg of DBP, 27.3 mg of PVC, 4.9 mg of L2 and 0.7 mg of NaTPB, in the case of L2 membrane). The uniform mixtures were then completely dissolved in 2 mL of THF. A Pyrex tube (3 mm i.d.) was dipped into each resulting solution for a few min. The tube was pulled out

from the solution and kept at room temperature for 1 h. The tube was filled with internal filling solution (1.0×10^{-3} M potassium chloride). The electrode was finally conditioned for 18 h by soaking in a 1.0×10^{-3} M KCl solution. A silver/silver chloride coated wire was used as an internal reference electrode.

Emf Measurements

All emf measurements were carried out with the following cell assembly:

Ag-AgCl / internal solution (1.0×10^{-3} M KCl)/PVC membrane / test solution / Hg-Hg₂Cl₂, KCl (satd)

A model 624 Metrohm digital research pH meter was used for the potential measurements. The emf observations were made relative to a double junction saturated calomel electrode (SCE, Philips) with the chamber filled with an ammonium nitrate solution. The activities of the metal ions were based on the activity coefficient, γ , data calculated from the Debye-Hückel equation [22]:

$$\text{Log } \gamma = -0.511 z^2 \left\{ \frac{\sqrt{I}}{1 + 1.5 \sqrt{I}} - 0.2 I \right\}$$

where I is the ionic strength and z is the cation charge.

RESULTS AND DISCUSSION

The two poly(oxyethylene) derivatives L1 and L2 were incorporated into PVC membrane electrodes and the potential response of the membranes with respect to Na^+ , K^+ , Li^+ , Ca^{2+} , Ba^{2+} and Cd^{2+} ions were obtained. The potential responses of the electrodes are given in Fig. 1. The linear responses of both membranes containing L1 and L2 to K^+ ion, as indicated in Figs. 1A and 1B, appear to be promising for fabrication of potassium ion selective electrodes. This is due to selective complexation of the ligands with potassium ion and the fast complexation-decomplexation kinetics at the solution-membrane interface [2,5,16].

According to the results, the potassium selective electrodes based on L1 and L2 exhibit a linear response to the activity of K^+ ions within the concentration ranges of 3.1×10^{-5} - 2.7×10^{-1} M and 2.0×10^{-5} - 7.3×10^{-1} M K^+ with slopes of 61.8 ± 1.6 and 62.6 ± 1.4 mV per decade, respectively. Although the electrode containing L2 responded to Ba^{2+} with a quasi-Nernstian slope, the linear activity of the potential response was narrow (from 1×10^{-5} to 1.6×10^{-3} M).

Table 1: Effect of membrane composition on the potential response of the K^+ -ion selective electrodes based on L1 and L2.

Ligand	Composition (%)				NaTPB	Slope ^a (mV/decade)	Linear Range (M)
	No.	PVC	DBP	Ligand			
L1	1	28.5	69.5	1.96	-	57.6	$2.0 \times 10^{-4} - 1.1 \times 10^{-1}$
	2	27.7	67.5	4.8	-	53.6	$3.1 \times 10^{-4} - 2.7 \times 10^{-1}$
	3	26.5	65.6	7.2	0.7	63.2	$3.1 \times 10^{-5} - 2.7 \times 10^{-1}$
	4	27.4	67.1	4.8	0.7	61.8	$3.1 \times 10^{-5} - 2.7 \times 10^{-1}$
	5	28.2	69.4	1.9	0.5	57.7	$2.0 \times 10^{-4} - 1.1 \times 10^{-1}$
L2	1	28.7	69.4	1.9	-	58.7	$2.1 \times 10^{-4} - 1.1 \times 10^{-1}$
	2	27.5	67.7	4.8	-	59.3	$3.1 \times 10^{-4} - 1.1 \times 10^{-1}$
	3	27.1	66.8	4.7	1.4	64.8	$2.0 \times 10^{-5} - 7.3 \times 10^{-1}$
	4	27.3	67.1	4.9	0.7	62.6	$2.0 \times 10^{-5} - 7.3 \times 10^{-1}$
	5	26.7	65.3	7.2	0.7	63.4	$3.1 \times 10^{-5} - 7.3 \times 10^{-1}$

(a) SD of the data was at the most ± 1.0 mV/decade.

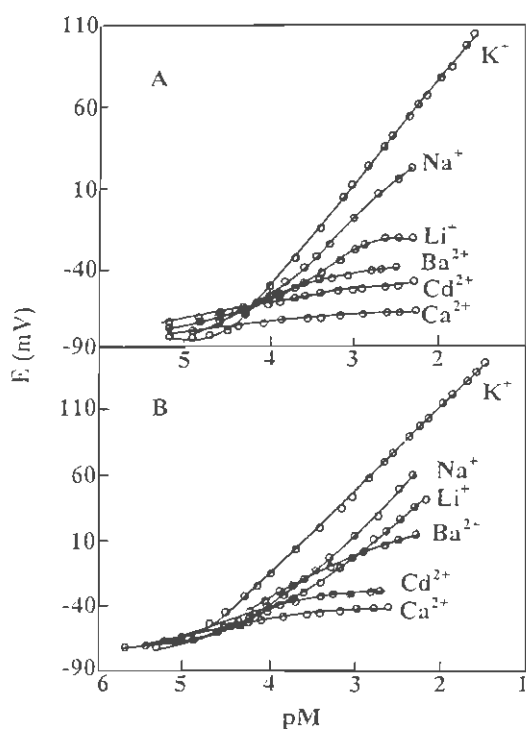


Fig. 1: Potential responses of various metal ion-selective electrodes based on L1 (A) and L2 (B)

It is well known that the sensitivity and selectivity obtained for a given ionophore depend significantly on

the membrane composition and nature of additives used [23-25]. Thus, the influences of the membrane composition and amount of sodium tetraphenylborate as a lipophilic additive on the potential response of the K^+ sensors based on the L1 and L2 were investigated, and the results are summarized in Table 1. Based on previous studies carried out on the preparation of K^+ ion-selective electrodes [3-18], in this work, we used DBP as a suitable solvent mediator. Table 1 show that, in the case of both ionophores, the composition number 4 resulted in the best performance of the K^+ -selective membranes. It should be noted that the presence of lipophilic anions in cation-selective membrane electrodes not only diminishes the ohmic resistance [23] and enhances the response behavior and selectivity [24] but also, in cases where the extraction capability is poor, increases the sensitivity of the membrane electrodes [25]. As can be seen from Table 1, in both electrodes based on L1, and L2, the presence of about 0.7% of NaTPB improves the linear range, sensitivity and emf stability of the resulting membrane electrodes [26]. The static response time of the sensors based on L1 and L2 was found to be 25 s and 30 s, respectively, over the entire concentration range. This is actually the average time required for the electrode to reach a potential within ± 1 mV of the final equilibrium value after suc-

cessive immersion of a series of K^+ ions, each having 10-fold difference in concentration [27]. The standard deviation of ten replicate potential measurements with the two sensors was ± 5 mV. The limit of detection of electrodes based on L1 and L2 was 2.0×10^{-5} and 1.5×10^{-5} M, respectively, as determined from the intersection of the two extrapolated segments of the calibration graphs.

The proposed electrodes were also used at different concentrations of the internal reference solution. The KCl concentration was changed from 1.0×10^{-4} to 1.0×10^{-2} M and the emf-pK⁺ plots were obtained. It was found that the variation of the concentration of the internal K^+ solution does not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting calibration plots. A 1.0×10^{-3} M concentration of the reference solution is quite appropriate for smooth functioning of the system.

The optimum conditioning time for the membrane electrodes in a 1.0×10^{-2} M KCl was 18 h, after which they generate stable potentials in contact with potassium solutions.

The pH response profiles for electrodes were examined by using 10^{-3} and 10^{-4} M KCl solution and the results are shown in Fig. 2. As seen, both electrodes gave a useful pH range of 3.5-11.0. At pH ≤ 2 , the potential increased, indicating that the electrode responded to hydrogen ion, while above pH 11.0, the potential change may be due to the formation of deprotonated forms of the ligands, as well as the increased interfering effect of NH_4^+ ion in the ammonium hydroxide solution used for the adjustment of pH of the test solutions.

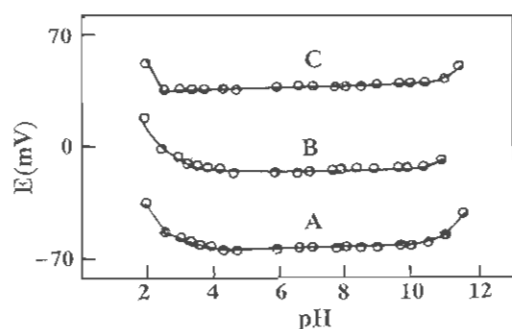


Fig. 2: Effect of pH on the potential responses of the selective electrodes based on L1 and L2: (A) L1, 1.0×10^{-4} M KCl; (B) L2, 1.0×10^{-4} M KCl; (C) L2, 1.0×10^{-3} M KCl

Table 2: Selectivity coefficients of various interfering ions for K^+ -ion selective electrodes based on L1 and L2.

Cation	$K_{A,B}^{Pot}$	
	L1	L2
Li^+	3.2×10^{-1}	2.4×10^{-1}
Na^+	1.0×10^{-1}	1.1×10^{-1}
Cs^+	7.3×10^{-1}	1.1×10^{-1}
NH_4^+	1.5×10^{-4}	1.8×10^{-4}
Mg^{2+}	5.5×10^{-4}	4.4×10^{-4}
Ca^{2+}	1.4×10^{-3}	6.3×10^{-4}
Sr^{2+}	4.8×10^{-4}	3.7×10^{-4}
Ba^{2+}	5.8×10^{-1}	8.9×10^{-1}
Ni^{2+}	5.6×10^{-4}	5.6×10^{-4}
Co^{2+}	8.5×10^{-4}	8.5×10^{-4}
Cd^{2+}	5.9×10^{-4}	5.9×10^{-4}
Cu^{2+}	1.3×10^{-3}	1.5×10^{-3}
$Fe^{3+}, Cr^{3+}, Mn^{2+}$	$< 10^{-4}$	$< 10^{-4}$

Perhaps the most important characteristic of a membrane sensor is its response for the primary ion in the presence of other cations. In order to assess the selectivity of the proposed potassium ion-selective electrodes over other cations, the method of fixed interference was employed [28]. According to this method, the potentiometric selectivity coefficients, $K_{A,B}^{Pot}$, can be evaluated from the potential measurements of solutions containing a fixed concentration of interfering ion, B^{n+} ($a_B = 5 \times 10^{-3}$ M) and titration with K^+ solution. The potential values obtained were then plotted against the activity of the potassium ion. The intersection of the extrapolated linear portions of this curve will indicate the activity of K^+ (a_A) which is to be used to calculate $K_{A,B}^{Pot}$ values from equation

$$K_{A,B}^{Pot} = \frac{a_A}{(a_B)^{2/n}} \quad (2)$$

The resulting $K_{A,B}^{Pot}$ values are summarized in Table 2. The results obtained show that the selectivity of the sensor with regard to alkali metal ions is in the order $K^+ > Cs^+ > Li^+ > Na^+$. Although the hydrophobicity and free energy of transfer (ΔG_t) data parameters of these metal ions are in the sequence $Cs^+ > K^+ > Na^+ > Li^+$ [29], selec-

Table 3: Alkali and alkaline earth content of the three water samples.

Sample	Concentration ($\mu\text{g/mL}$)									
	AAS									K ⁺ -ISE
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺	K ⁺
Tap water	n ^a	18.5	0.3	1.3	n	16.8	35.6	0.4	n	0.25 \pm 0.03
River water	n	38.1	0.7	1.5	n	18.2	56.0	0.6	n	0.65 \pm 0.05
Well water	n	41.3	0.9	1.4	n	15.8	71.5	0.9	n	0.88 \pm 0.06

^a n = negligible amount.

tive complexation of K⁺ ion with L1 and L2 displaces Cs⁺ in respect of the above order of hydrophobicity and the $\Delta G_r - K_{A,B}^{\text{Pot}}$ correlation is no longer valid. Accordingly, the selective response of L1 and L2 membranes towards K⁺ ion could be mainly explained in terms of selective K⁺-ligand interaction and a preferred extraction of K⁺ ion into the plasticized membrane phase.

The rejection of divalent alkaline earth and transition metal ions by the plasticized membranes is quite high. The selectivity coefficients of 10⁻³ and lower observed divalent metal ions used emphasize that they would not significantly disturb the functioning of the K⁺-selective membranes.

The utility, sensitivity and selectivity of the proposed membrane sensors were verified by determining 5 $\mu\text{g mL}^{-1}$ of K⁺ in synthetic mixtures containing 5-50 fold excess of different alkali and alkaline earth metal ions using the standard addition technique. Results with an average recovery of 99.0% and a mean standard deviation of 1.8% were obtained.

The proposed electrode containing L2 was also used to determine the potassium content of various water samples including tap water, spring water and river water. The water samples were first analyzed by AAS to determine their alkali and alkaline earth contents. The results are summarized in Table 3. Then the potassium content of water samples was determined by the membrane sensor using the standard addition method, and the results are also included in Table 3. As is obvious, there is a

satisfactory agreement between the results obtained by the proposed sensor and those by AAS.

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