

Potassium-Selective PVC Membrane Electrodes Based on Newly Synthesized *cis*- and *trans*-Bis(crown ether)s

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Ion-selective electrodes (ISEs) based on ionophore-impregnated polymer membranes for potassium ion (K^+) are steadily replacing flame photometry and other assay techniques for monitoring K^+ in various matrices and have been widely used in numerous analytical applications.¹ These ISEs incorporate neutral ionophores such as valinomycin (Fluka potassium ionophore I, Fig. 1)²⁻⁴, crown ether⁵⁻¹⁰ and recently rifamycin¹¹ as active membrane components. Among the reported ionophores, valinomycin is by far, the most successful ionophore for K^+ ion. However, valinomycin is a very expensive reagent with toxicity, and its membrane can be partially blocked by coexisting Cs^+ , Rb^+ and possibly NH_4^+ in the determination of K^+ .

The complexing properties of these so-called crown compounds have been dealt with in a large number of papers since they were first described by Pedersen.¹² Bis(15-crown-5 ether)s, which have two equivalent 15-crown ethers, are well known; these compounds form more stable complexes with potassium than with sodium and are considered as a cheap alternative to valinomycin. A large number of bis(crown ether)s have been synthesized and their potentiometric performances have been examined as mentioned earlier. The structure-selectivity relationship obtained with crown compounds of different ring sizes revealed that bis-crown ethers may have distinct advantages due to their binding affinities towards alkali metal cations by complexing ions forming 1:2 complexes with the relevant mono crown compounds. Simultaneously, it was expected that the two crown ether moieties in one molecule will increase the lipophilicity of the ligands and improve the kinetics of the complexation, *i.e.* the life and the response time of such ionophore-based sensors, respectively.

For the development of efficient ISEs and synthetic ion transporters, highly lipophilic molecules should be incorporated into crown ethers. Recently, Chung *et*

*al.*¹⁰ and Moriaty *et al.*¹³ reported that the rigid and compact hydrocarbons such as xanthene or cubane are more relevant for this purpose than commercially available long-chain hydrocarbons (Fluka potassium ionophore II; Fig. 1) that may increase lipophilicity but also decrease the mobility of the carrier.

Recently we reported the newly synthesized geometrical isomer of *cis*- and *trans*-bis(benzocrown ether)s (Fig. 1) which are derived from a new structurally well-

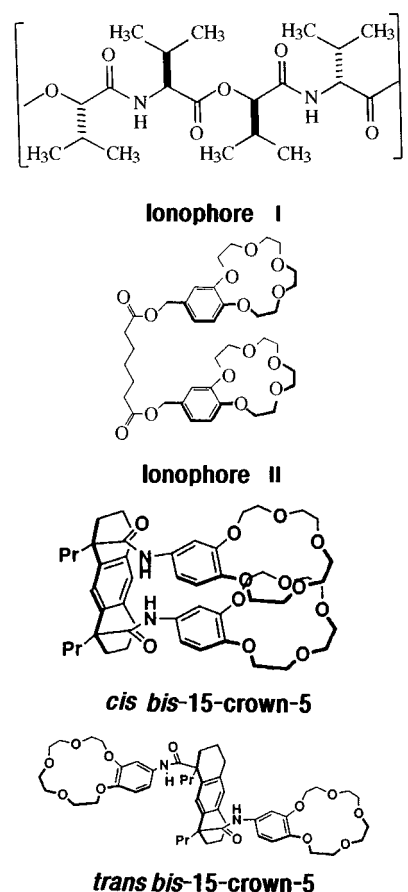


Fig. 1 The structure of potassium ionophores.

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defined molecule, 1,2,3,4,5,6,7,8-octahydro-1,8-dipropyl-1,8-dicarboxylic acid, and evaluated their cation-binding properties.¹⁴ Here, we report the potentiometric performances of two geometrical isomers of these bis(crown ether)s as a potassium sensor. We also evaluated the enhancement of potassium selectivity toward other cations according to complex-forming geometry.

Experimental

Reagents

Poly(vinyl chloride), potassium tetrakis(4-chlorophenyl)borate (KTPCIPB), *o*-nitrophenyl octyl ether (NPOE) and bis(2-ethylhexyl) sebacate (DOS) were purchased from Fluka (Ronkonkoma, NY). Valinomycin (potassium ionophore I) and bis[(benzo-15-crown-5)-4-ylmethyl] pomelate (potassium ionophore II) were also purchased from Fluka. The new *cis*- and *trans*-bis(benzocrown ether)s are synthesized from a new structurally well-defined molecule, 1,2,3,4,5,6,7,8-octahydro-1,8-dipropyl-1,8-dicarboxylic acid, through a published method.¹⁴ All other chemicals used were of analytical reagent grade. Standard solutions and buffers were prepared with the use of deionized water.

Preparation and evaluation of polymer membranes and electrode

PVC matrix membranes were prepared according to the method reported previously.¹⁵ The composition of PVC-based cation selective membrane was 1wt% ionophore, 33wt% PVC and 66wt% plasticizer with a total weight of 200 mg. The detailed compositions of membranes used in this experiment are listed in Table 1. The membranes were prepared by dissolving the mixture in 5 ml of THF. In each case, after curing, small disks (5.5 mm) were punched from the cast films and mounted in Philips electrode bodies (IS-561; Glasblaserei Müller, Zürich, Switzerland). A certain

amount of the lipophilic additive reagent was added to the membrane mixtures mentioned earlier in this section.

The potentiometric behavior of the membrane electrodes was evaluated with conventional ISE configuration. For all electrodes, 0.1 M KCl was employed as the internal filling solution. The external reference electrode was an Orion sleeve-type double junction Ag/AgCl electrode (Model 90-02). Electrodes were connected through a high impedance amplifier to an IBM AT-type computer equipped with an analog-to-digital converter. The cell potential were measured at ambient temperature (25°C) by immersing ISEs and the reference electrode in a beaker containing 200 ml of the working buffer (0.05 M Tris-HCl, pH 7.2); the calibration data were obtained from additions of standard solutions. The solutions were magnetically stirred throughout and equilibrium potentials were recorded. Selectivity coefficients were estimated according to the separated solution-matched potential method at an interfering cation concentration of 0.1 M.¹⁶ The detection limits of the membrane electrodes were obtained from the calibration plots following the recommended procedure.¹⁷ The response of an electrode toward pH was obtained by titrating a universal buffer of pH 2.8 (11.4 mM boric acid; 6.7 mM citric acid; 10.0 mM sodium dihydrogen phosphate) with small aliquots of LiOH, while simultaneously monitoring the pH of the sample solution with a combination glass pH electrode.

Results and Discussion

The potentiometric behavior of potassium ionophores I (valinomycin) and II from Fluka and newly synthesized bis(15-crown-15 ether)s with conventional membrane composition was investigated. Among the reported ionophores, valinomycin (membrane **A**) is by far, the most successful ionophore for K⁺ ion. The *cis*-bis(15-crown-5 ether) based membrane (membrane **C**) exhibited the same potentiometric responses or better ones than valinomycin-based one (membrane **A**) as a potassium sensor. For instance, membrane **C** exhibits Nernstian potentiometric behavior (59.0 mV/dec) and excellent detection limit (9.5×10⁻⁷ M) for K⁺-like membrane **A** (1.3×10⁻⁶ M). This preliminary potentiometric test indicates that membrane **C** shows highly selective performance against the applied monovalent cations (log K_{K⁺,j⁺}^{pot}: Li⁺, -4.07; Na⁺, -3.69; NH₄⁺, -2.28; Rb⁺, -1.26; Cs⁺, -2.25) and Ca²⁺ ion (no response). Those selectivities are very comparable (log K_{K⁺,j⁺}^{pot}: Li⁺, -4.19; Na⁺, -4.67; NH₄⁺, -1.88) to membrane **A**, and better for relatively bigger monovalent cations (Rb⁺, 0.41; Cs⁺, -0.31) and Ca²⁺ ion (-3.20). *trans*-Bis(15-crown-5 ether) based membrane (membrane **D**) also exhibited good performance (detection limit, 1.3×10⁻⁶ M; K_{K⁺,j⁺}^{pot}: Li⁺, -3.94; Na⁺, -3.14) as K⁺-ion-selective membrane, but selectivities to ammonia (-1.42), Rb⁺ (-0.40), Cs⁺ (-1.14) and Ca²⁺ (-3.19) are not as good as for mem-

Table 1 The compositions of potassium-selective membranes

	A	B	C	D
Ionophore (1wt%)	Ionophore I ^a	Ionophore II ^b	<i>cis</i> bis-15-crown-5	<i>trans</i> bis-15-crown-5
Matrix (33wt%)	PVC ^c	PVC	PVC	PVC
Plasticizer (66wt%)	DOS ^d	DOS	NPOE ^e	NPOE

a. Valinomycin.

b. Bis[(benzo-15-crown-5)-4-ylmethyl] pimelate.

c. Poly(vinyl chloride) high molecular weight.

d. Bis(2-ethylhexyl) sebacate.

e. 2-Nitrophenyl octyl ether (the membranes with NPOE exhibits similar potentiometric performance to potassium ion to that of the membrane with DOS).

Table 2 The effects of addition of lipophilic anionic additive to potentiometric performances by *cis*-bis(15-crown-5 ether) based membrane

Ionophore <i>cis</i> 15-crown-5	Maximal slope/ mV dec ⁻¹	Selectivity coefficient log $K_{K^+}^{pot}$					Detection limit/ M
		Li ⁺	Na ⁺	NH ₄ ⁺	Rb ⁺	Cs ⁺	
Lipophilic additive 0%	59.0	-4.07	-3.69	-2.28	-1.26	-2.25	-6.02
Lipophilic additive 100%	59.0	-4.16	-3.48	-2.30	-1.07	-2.73	-6.37

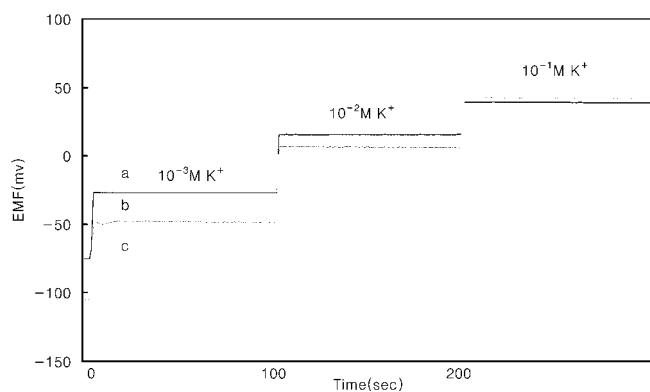


Fig. 2 The effects of addition of lipophilic anionic additive to potentiometric performances by *cis*-bis(15-crown-5 ether) based membrane. The composition of membrane **C** (Table 1) with addition of KTpCIPB: a) 0 mol%; b) 50 mol%; c) 100 mol% to ionophore.

brane **C**. Both membranes based on newly synthesized bis(15-crown-5 ether) exhibit slightly better performance than commercially available bis(15-crown ether) (membrane **B**) (detection limit, 1.3×10^{-6} M; $\log K_{K^+}^{pot}$: Li⁺, -3.30; Na⁺, -3.10; NH₄⁺, -1.82; Rb⁺, -0.90; Cs⁺, -2.05; Ca²⁺ ion, -3.68).

Newly synthesized *cis*- and *trans*-bis(15-crown-5 ether) have the identical molecular components but their geometries are different from each other. They are expected to show structural advantages due to the improvement in preorganization property in comparison with a commercial ionophore such as potassium ionophore I and II, because the bridge between the two crown ethers is solidified. In the previous report¹⁴, all observations in extraction experiments indicated that intramolecular sandwich type 1:1 complex could be formed in the *cis* isomers, regardless of metal cation sizes. When the ratio of the cation size and cavity size is >1, extraction by the *cis* isomers occurs either completely or at least predominantly *via* the stable 1:1 complex. The higher polarity of the *cis* compound than of the *trans* one may lead to the higher metal ion extractability. However, the potentiometric behavior as potassium sensor is similar for the two membranes **C** and **D**, in spite of the huge difference of extractabilities (87% for K⁺ by *cis* compound and 21% by *trans* compound). Measurements of pH dependence were made using the crown ether-based membranes. The emf remains constant in the pH range 3 to 11 for all

membranes. The small variations of potentiometric responses for membrane **B** and **D** were not significant enough to affect the analytical results.

At 25°C, potassium sensor, the membrane **C** displayed an excellent overall performance with the detection limit of less than 10^{-6} M. However, the calibration slope was substantially decreased at the potassium concentration over 10^{-2} M (Fig. 2, trace a). This phenomenon is probably due to interfacial kinetic limitations in the transfer of ions from the membrane surface to the liquid membrane phase at the high activity of K⁺ and is usually fixed by addition of lipophilic additives because lipophilic anionic components can efficiently catalyze this cation transfer.¹⁹ Thus we added KTpCIPB as the anionic membrane component. The effect of the amount of KTpCIPB as the anionic additive in the electrode membrane on the potentiometric feature was examined with membrane **C**. In general, the addition of the anionic additive causes positive emf response behavior, for instance, reduction of anionic interference at high sample activities. As seen in Fig. 2, emf responses over 10^{-2} M of K⁺ ion concentration are dramatically improved to near Nernstian (56 mV/dec) potentiometric behavior with addition of KTpCIPB over 100 mol% to ionophore. The larger amount of KTpCIPB against the ionophore content leads to the more reduced anionic interference at high sample concentration. The addition of anionic additive did not cause any significant potentiometric performance changes (Table 2).

Thus, the valinomycin-based PVC membrane (membrane **A**) has been proved to be an excellent K⁺ ion-selective electrode as superior response toward Na⁺ ion. However, because valinomycin is relatively expensive and toxic, the overall performances of membrane **C**, newly synthesized *cis*-bis(15-crown-5 ether) compound, can definitely be considered as an alternative as a K⁺ ion selective ionophore for various purposes.

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