

New Potassium-Selective Electrode Based on an Ionophoric Bis(15-crown-5 ether) Derived from Xanthene-4,5-Dicarboxylic Acid

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Bis(15-crown-5 ether) derivatized from a xanthene-4,5-dicarboxylic acid skeleton was studied as an ionophore for a new K⁺-selective electrode. The polymeric liquid membrane based on this ionophore exhibits Nernstian behavior and optimization of experimental conditions for potentiometric analysis offers a wide linear dynamic range, reasonable detection limit, good durability and hysteresis within a limited error. Due to the well-preorganized structure, the selectivity over Na⁺ is comparable to those of commercialized K⁺-selective ionophores and the interferences by some cations such as Rb⁺ and Cs⁺ are reduced. Except slightly slow response, the enhanced recognition ability is reminiscent of the natural antibiotic valinomycin.

Keywords Bis(15-crown-5 ether), potassium ion-selective electrode, potentiometric analysis

Bis(15-crown-5 ether)s, which have two equivalent 15-crown-5 ethers, are well-known strategy to replace the natural K⁺-selective ionophore, valinomycin, for the development of improved K⁺-selective electrode (K⁺-ISE).¹ In this system, the geometry and spatial arrangements of two crown ether moieties are crucial factors to exhibit efficient ionophoric activity.^{2,3} L1 and L2 in Fig. 1 are synthetic K⁺-selective ionophores which were developed by Kimura *et al.*³ and Lindner *et al.*⁴, respectively. They are representative biscrown ether type K⁺-selective ionophores that their ionophoric activities are comparable to valinomycin and thus were commercialized by Fluka. On the other hand, L3 is a bis(15-crown-5 ether) derivatized from xanthene-dicarboxylic acid that was reported as a motif for the construction of a rigid host framework by Rebek.⁵ Three reasons can be suggested to explain why this new motif, xanthene-dicarboxylic acid, was incorporated into the conventional biscrown ether structure as a spacer in this study. The first one is that the introduction of xanthene-dicarboxylic acid is expected to create more preorganized framework and the second one is that

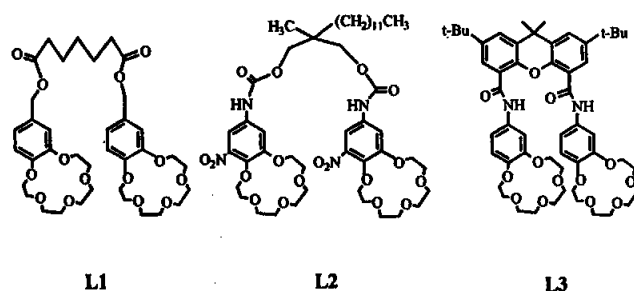


Fig. 1 Structures of K⁺-selective bis(15-crown-5 ether)s.

the two *tert*-butyl groups as well as the xanthene backbone is lipophilic enough to be utilized as a sensing material in polymeric liquid membrane. The last one is that L3 suggests a fluorescent biscrown ether type ionophore because xanthene moiety can act as an energy mediator.⁶ Extraction, ion transport experiments and preliminary potentiometric test indicate that L3 shows highly selective affinity to potassium ion and exhibits Nernstian potentiometric behavior.⁷ In this report, optimal experimental conditions of poly(vinyl chloride)(PVC) supported liquid membrane based on L3 are determined for

potentiometric analysis of potassium ion. In addition, L3 is compared with commercialized ionophores in terms of selectivity over interferents as well as basic sensing properties, and other characteristics of the membrane are described.

Experimental

Reagents

All plasticizers, electrode body and implements for casting membrane were purchased from Fluka. Sodium dipicrylamine (NaDPA, Tokyo Chemical Industry Co.) and potassium tetrakis(4-chlorophenyl) borate (KTPCIPB, Fluka) were added as lipophilic salts. Li^+ , Na^+ , Sr^{2+} , Ba^{2+} , NH_4^+ (+99.9%, Junsei Chemical Co.), K^+ , Rb^+ , Cs^+ , Mg^{2+} and Ca^{2+} (+99.9%, Aldrich) salts were used without further purification and all salts were chlorides.

Apparatus

Potential measurements were carried out with a home-made data acquisition set-up that consists of a terminal circuit and a 12 bit analog to digital converter (MC-MIO-16, National Instruments Co.) connected to a personal computer (IBM PS2). In order to enhance the input impedance, 8 parallel voltage followers and preamplifier circuits were used as potentiometer terminals. The system of the cell is $\text{Ag}|\text{AgCl}|3\text{ M KCl}||0.05\text{ M Tris-HCl}||\text{sample}, 0.05\text{ M Tris-HCl}|\text{membrane}|0.01\text{ M KCl}|\text{AgCl}|\text{Ag}$.

Preparation of liquid polymeric membranes

The preparation of liquid membranes based on Fluka potassium ionophore II (L1) and III (L2) was followed to the corresponding literatures.^{3,4} The composition of valinomycin (potassium ionophore I, Fluka)-based membrane was 2 mg of ionophore, 66 mg of PVC and 132 mg of *o*-nitrophenyl octyl ether (*o*-NPOE). PVC and ionophore were dissolved by adding 1 mL of tetrahydrofuran (THF) to the mixed powder in a test tube. Plasticizer was added to the absolutely transparent solution and stirred vigorously for overnight. Then this mixture was poured into a cylindrical tube with 25.5 mm i.d. on a petri dish and dried for 24 h.

Ion-selective electrode (ISE) tests

The response to the primary ion was measured by immersing eight electrodes into 250 mL of background solution. The concentration of the primary ion increases quantitatively. The selectivity

coefficients for K^+ were determined by fixed interference method (FIM).⁸ In the determination of selectivity coefficients by FIM, the concentrations of interferents were 5.0×10^{-2} M, 5.0×10^{-2} M, 1.0×10^{-3} M, 5.0×10^{-3} M and 5.0×10^{-3} M for Li^+ , Na^+ , Rb^+ , NH_4^+ and Cs^+ , respectively. The concentration of all alkaline earth metal ions was 1.0×10^{-2} M. The interference by H^+ was investigated in universal buffer ($\mu=0.05$), which was composed of boric acid 11.4 mM, citric acid 6.7 mM and phosphoric acid 5.0 mM. The pH was varied from 2.7 to 10.6 by adding appropriate quantity of 3 M LiOH. The detection limit was measured according to the literature.⁸ The concentration was changed when 60 seconds elapsed after the previous change and data points were read for every second. The raw data of potential response were acquired at from 40 to 50 seconds after every concentration change and were averaged to be used for final calculations. The recovery test or hysteresis test was performed according to the procedure as follows. Firstly, the potentials were measured when the concentration increased by a half decade. Secondly, the solution was diluted following reverse steps; removing calculated volume out of sample solution with pipettes and pouring 100 mL of background buffer solution into the cell. The resistances of liquid membranes were measured according to the literature.⁹ The temperature of the solution was controlled by circulating water through water jacket around the cell with thermostat (Model B, Lauda-Königshofen, Germany). All experiments were performed in 0.05 M Tris-HCl buffer of pH 7.2 at 20 °C except the measurement of H^+ interference.

Results and Discussion

Effect of membrane components

In order to establish the optimal condition for practical analysis, various factors such as plasticizer, membrane composition and lipophilic salts on ISE function were investigated systematically. Table 1 shows potentiometric properties of membranes with different plasticizers where the composition is fixed at conventional one, ionophore : PVC : plasticizer = 1 : 33 : 66. Although the polar plasticizer of *o*-NPOE exhibits the best characteristics in terms of lowest detection limit and excellent selectivity coefficients, the slope of response to K^+ ion is noticeably poor. As described in the last section, this low sensitivity can be overcome by increasing the temperature of sample solution to about 37 °C. However, there is a serious drawback in the case of practical

Table 1. Optimization of liquid polymeric membrane for K⁺-selective electrode based on L3

	Plasticizer ^a				Composition ^b		Lipophilic salt ^c	
	o-NPOE	DOS	DBP	TEHP	0.5:33:66	2:33:66	KTpCIPB	NaDPA
Maximal slope (mV/decade)	45	56	54	56	56	56	57	57
Linear response range (M) ^d	3 × 10 ⁻⁵ ~ 1 × 10 ⁻²	1 × 10 ⁻⁴ ~ 3 × 10 ⁻²	3 × 10 ⁻⁵ ~ 1 × 10 ⁻²	1 × 10 ⁻⁴ ~ 3 × 10 ⁻²	3 × 10 ⁻⁵ ~ 3 × 10 ⁻²	3 × 10 ⁻⁵ ~ 3 × 10 ⁻²	3 × 10 ⁻⁵ ~ 3 × 10 ⁻²	3 × 10 ⁻⁵ ~ 3 × 10 ⁻²
Detection limit (x 10 ⁻⁶ M)	3.5	5.6	4.8	8.0	5.6	6.0	5.5	5.5
log K ^{pot} _{K⁺,M}								
H ⁺	-1.6	-1.6	-1.6	-1.4	-1.2	-1.2	-1.4	-1.4
Li ⁺	-3.5	-3.3	-3.4	-3.1	-3.6	-3.6	-3.3	-3.3
Na ⁺	-3.7	-3.5	-3.5	-3.3	-3.5	-3.5	-3.4	-3.4
Rb ⁺	-1.3	-1.0	-1.2	-1.0	-0.8	-0.8	-0.9	-0.9
Cs ⁺	-1.8	-1.7	-1.8	-1.7	-2.4	-2.4	-2.4	-2.4
Mg ²⁺	-4.0	-3.8	-3.9	-3.8	-4.0	-4.0	-4.3	-4.3
Ca ²⁺	-3.6	-3.5	-3.5	-3.5	-4.3	-4.3	-4.4	-4.4
Sr ²⁺	-3.8	-3.6	-3.7	-3.6	-3.8	-3.8	-3.4	-3.4
Ba ²⁺	-3.8	-3.7	-3.7	-3.7	-4.2	-4.2	-4.2	-4.2
NH ₄ ⁺	-3.3	-2.0	-2.1	-2.0	-2.1	-2.1	-2.2	-2.3

a. The composition is L3 : PVC : plasticizer = 1 : 33 : 66 (wt/wt).

b. The plasticizer is DOS.

c. The composition is L3 : PVC : plasticizer : lipophilic salt = 0.5 : 33 : 66 : 0.2 (wt/wt).

d. The concentration range in which square of correlation coefficient exceeds 0.999.

analysis at room temperature. On the whole, membranes based on dioctyl sebacate (DOS), dibutyl phthalate (DBP) and tris(2-ethylhexyl) phosphate (TEHP) exhibit similar properties. DOS gives the most stable and reproducible response in comparison to the other two plasticizers. As a result, DOS seems the best plasticizer for sensitivity and reproducibility whereas o-NPOE is the most suitable one for detection limit and selectivity.

Quantitative variation of ionophore from 0.5 mg to 2 mg leads to no significant difference as the same composition of PVC and plasticizer is maintained. Table 1 indicates that the addition of lipophilic salts does not affect any notable change in membrane properties. Therefore, ionophore : PVC : DOS = 0.5 : 33 : 66 (wt.) without lipophilic salt is found to be the most acceptable composition with respect to the function as an ISE and convenience in membrane fabrications, and was used in the following comparison study.

Comparison with commercial ionophores

L3 is expected to show structural advantage due to the improvement in preorganization property in comparison with the commercial ionophores such as K⁺-ionophore I (valinomycin), II (L1) and III (L2) from Fluka because the bridge between two legs is

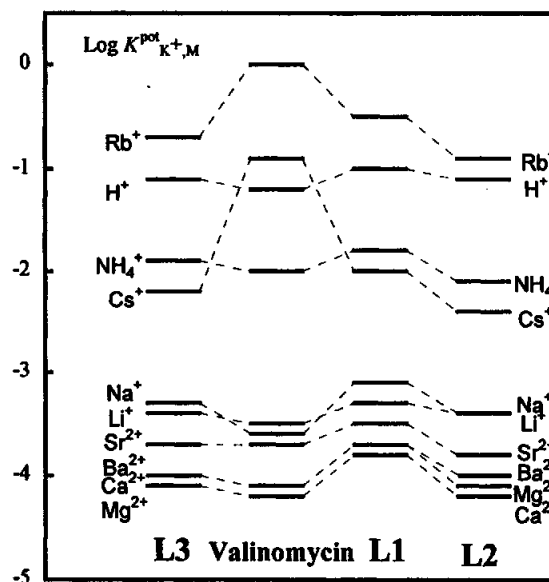


Fig. 2 Selectivity coefficients for K⁺ of liquid membranes based on L3 and commercial ionophores. DOS was used as plasticizer for the L3-based membrane.

solidified. Fig. 2 displays selectivity coefficients of these four ionophores. With regard to selectivity for K⁺ over Na⁺, valinomycin is the best and L3 shows a similar result compared to L2. Against Rb⁺ and Cs⁺, L3 is found to be superior to valinomycin or L1

while it is less selective than L2. Over other interferents, L3 exhibits almost comparable selectivity to commercial ionophores. If a little disadvantage in sensitivity is tolerable as indicated in Table 1, selectivities over all interferents can be improved by using o-NPOE as a plasticizer.

Dynamic properties

Since L3 is fairly well-preorganized in its shape, a retardation of potentiometric response to activity steps is questionable. Fig. 3 shows potential jumps of L3- and L2-based membranes upon an increase in the concentration of potassium ion by a half decade. Because t_{90} is evaluated on the basis of the data in calibration curve, it is not a response time in strict meaning.¹⁰ But these values reveal relative response rates of tested membranes and thus imply that the response of L3-based membrane is somewhat slower than that of the membrane based on L2. This small retardation in response is reduced as the temperature increases and eventually no difference between the response speeds of L3 and of valinomycin, L1 and L2 is observed at 37 °C. Supposedly, this phenomenon reflects the rigid structure of L3 that stems from a stiff spacer, xanthene-dicarboxylic acid.

Resistances of liquid membranes can provide an information about the dynamic property of an ionophore in the interface between lipophilic

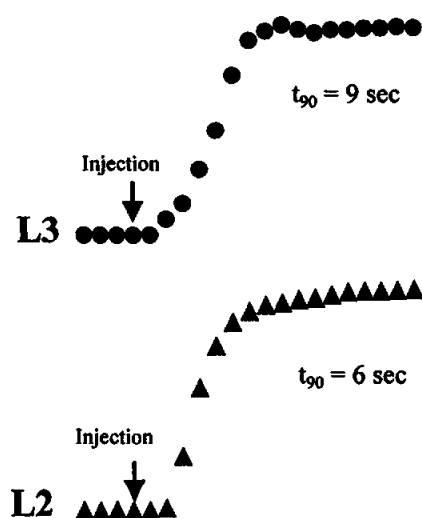


Fig. 3 Potentiometric responses to the concentration step of K^+ from 3.0×10^{-4} M to 1.0×10^{-3} M.

membrane and aqueous phase. Resistances of the membranes based on valinomycin, L1, L2 and L3 are 0.77, 0.31, 0.25 and 0.61 $M\Omega$, respectively, which are less than 1 $M\Omega$. Therefore, all ionophores in this study are supposed to maintain thermodynamic equilibrium reversible enough to give rapid and stable responses to the activity changes. As for reproducibility and durability of ISE based on L3, repeated increase and decrease of the concentration of potassium ion indicate negligible hysteresis and all sensing properties without any noticeable deterioration for more than four weeks.

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