Structural Effect of Several Acyclic Neutral Carriers Containing 8-Quinolyloxy Units on the Stability Constants of Their Li⁺ Complexes in Water-Saturated Nitrobenzene

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The stability constants ($\beta_1^{\text{NB}}(\text{M})/\text{mol}^{-1} \text{dm}^3$) of 1:1 complexes of M^+ ($=\text{Li}^+, \text{Na}^+$) with 1,3-bis(8-quinolyloxy)propane (IV), 1,4-bis(8-quinolyloxy)butane (V) and 3,3-bis[(7-methyl-8-quinolyloxy)methyl]oxetane (VI) were determined by ion-transfer polarography in water-saturated nitrobenzene (NB) at 25°C. Their logarithmic values were on the order of VI (4.6) < V (5.7) < IV (7.4) for $\text{M}=\text{Li}$ and VI (3.9) < V (4.5) < IV (5.7) for $\text{M}=\text{Na}$. This order shows that the stability of the Li^+ and Na^+ complexes significantly increases when the carrier can form a four-coordinate structure similar to that of a tetradentate 14-crown-4 in their complexes. The potentiometric selectivity coefficients ($k_{\text{LiNa}}^{\text{pot}}$) of IV–VI for Li^+ against Na^+ were calculated based on the $\beta_1^{\text{NB}}(\text{M})$ -values using the equation $\log k_{\text{LiNa}}^{\text{pot}} = 0.70 + \log[\beta_1^{\text{NB}}(\text{Na})/\beta_1^{\text{NB}}(\text{Li})]$, and the results compared with those previously described for other bis(8-quinolyloxy)propane derivatives.

Keywords Stability constant, Li^+ selectivity, bis(8-quinolyloxy)alkane, water/nitrobenzene interface, ion-transfer polarography

Considerable attention has been focused on Li^+ -selective electrodes as a tool for the potentiometric determination of Li^+ activity in biological and environmental samples.¹ In monitoring the Li^+ activity during therapy for manic-depressive illness^{1b}, a high Li^+ selectivity of the ion-selective electrodes (ISEs) is required because of interference from Na^+ which appears in high concentrations in body fluids. Kimura *et al.*² applied 14-crown-4 (14C4) compounds to neutral carriers of liquid membrane-type ISEs and achieved high Li^+ selectivity over Na^+ and K^+ . Recently, Hiratani *et al.*³ designed a series of acyclic compounds for neutral carriers (L, Fig. 1) to Li^+ -selective electrodes, and then examined potentiometrically the Li^+ selectivity of liquid membrane-type ISEs with carriers I–VI. Especially, the Li^+ selectivity of ISEs with carriers I and II was comparable to that of ISEs with commercially-available 14C4 derivatives, such as dibenzyl-14C4 (DBz14C4) and phosphododecyl-14C4.^{2,4a} In view of the modification of acyclic L for improving the Li^+ -selective electrode, it is interesting to study how the structure of L enhances the stability of its Li^+ complex.

In the present study, we determined the stability constants of complexes of three acyclic neutral carriers (IV–VI) with Li^+ and Na^+ in a water-saturated nitrobenzene (NB) solution using the ion-transfer polarographic method, and calculated the potentiometric selectivity coefficients of IV–VI for Li^+ over Na^+ based

on their stability constants. On the basis of these results, the structural effect of the six carriers (I–VI) on the stability constants are discussed.

Fig. 1 Structural formulas of carriers I–VI employed.

Experimental

Chemicals

Three carriers {1,3-bis(8-quinolyloxy)propane (IV), 1,4-bis(8-quinolyloxy)butane (V) and 3,3-bis[(7-methyl-8-quinolyloxy)methyl]oxetane (VI)} were synthesized by a previously reported method.³ All other chemicals were of analytical grade and were used without further purification. The method of preparing all of the solutions used was the same as that described in a previous paper.^{4a}

Electrochemical measurements

The electrolytic cell with an electrolyte dropping electrode was the same as that described in a previous paper.⁵ The cell temperature was controlled at $25.0 \pm 0.5^\circ\text{C}$ by circulating thermostated water through the jacket. A galvanic cell with the following characteristics was employed for controlling the measurements of the potential difference at the water (w)/NB-interface:

Here, the test interface is indicated by an asterisk and TBA·TPB denotes tetrabutylammonium tetraphenylborate as a supporting electrolyte in the NB-phase. The symbol c_M ($0.03 - 0.7 \text{ mol dm}^{-3}$) represents the bulk concentration of the metal (M) ion in the w-phase, which is in large excess compared with the concentration of L in the NB-phase. The pH values of the w-phases containing either LiOH or NaOH were in the 8.8 to 11.8 range. All other procedures were the same as those described previously.^{4a,5} The values of the potential ($\Delta\phi$) given in the present work were calculated in the same way as before⁵, and are designated as $V \text{ vs. TPh(As/B)E}$ (the $\text{Ph}_4\text{As}^+\text{BPh}_4^-$ electrode).

Results and Discussion

Representative polarograms for the Li^+ - and Na^+ -IV systems are shown in Fig. 2. Well-defined facilitated waves were observed in the range of 0 to $+0.2 \text{ V vs. TPh(As/B)E}$; their diffusion-controlled limiting currents changed in proportion to the bulk concentration of IV. A log-plot analysis of the current-potential curves yielded straight lines with reciprocal slopes of $60 \pm 1 \text{ mV/decade}$ for the Li^+ -IV system ($n=15$) and 59 ± 1 for the Na^+ -IV system ($n=13$). Similar results were also obtained for the other systems; the reciprocal slopes were

Fig. 2 Representative polarograms of $0.244 \text{ mol dm}^{-3} \text{ Li}^+$ and $0.214 \text{ mol dm}^{-3} \text{ Na}^+$ in the presence (curve a) and absence (b) of $0.372 \text{ mmol dm}^{-3}$ IV in the NB-phases. The reciprocal slopes = 60 mV/decade (Li) and 59 (Na); the half-wave potentials = -11 mV (Li) and 55 (Na).

Fig. 3 Plots of $\Delta\phi_{1/2}$ vs. $\log c_M$ for carriers IV-VI. M: Li (open symbols); Na (solid symbols). The slopes of the straight lines: -62 mV/decade for the Li^+ -IV system (symbol: $\diamond$); -56 for Na^+ -IV ($\blacklozenge$); -58 for Li^+ -V ($\circ$); -54 for Na^+ -V ($\bullet$); -61 for Li^+ -VI ($\triangle$) and -59 for Na^+ -VI ($\blacktriangle$).

Fig. 4 Plots of F_A vs. $1/c_M$ for the IV systems.

59±0.4 mV/decade for the Li⁺-V system (10), 58±2 for Na⁺-V (10), 56±3 for Li⁺-VI (11) and 57±3 for Na⁺-VI (8). These results indicate that the facilitated waves are reversible and diffusion-controlled, and are caused by a transfer of a univalent cation across the w/NB-interface.⁵ Figure 3 shows half-wave potentials ($\Delta\phi_{1/2}$) which depend on the logarithmic values of the Li⁺ and Na⁺ bulk concentrations. The slopes of the straight lines in Fig. 3 demonstrate that carriers IV–VI react with Li⁺ and Na⁺ to form only 1:1 complexes in the water-saturated NB-phase.⁵

As described in a previous paper⁵, the function F_A ($=\exp[(zF/RT)(\Delta\phi_{1/2}-\Delta\phi_M^0)]$) was plotted against $1/c_M$ (Fig. 4), where $\Delta\phi_M^0$ denotes the ion-transfer formal potential of the simple metal ion across the w/NB-interface: $\Delta\phi_{Li}^0=0.395$ V and $\Delta\phi_{Na}^0=0.354$ V vs. TPh(As/B)E.⁶ The plots yielded straight lines passing through the origin within the experimental errors. We can readily calculate the stability constants of 1:1 complexes in the water-saturated NB-phase from the slopes of the straight lines in Fig. 4, because the condition that carriers IV–VI possess high hydrophobic properties is satisfied.^{4a} Table 1 lists the stability constants ($\beta_1^{NB}(M)$, M=Li and Na) of the complexes with IV–VI, together with those of the 1:1 complexes with the previously reported carriers I–III.^{4a}

The sequences of the β_1^{NB} -values are IV>III>II>I>V>VI for the Li⁺ complexes and IV>III>V>I>II>VI for the Na⁺ complexes. A comparison of these two sequences indicates that an increase in the β_1^{NB} -values of the Li⁺ complexes due to a modification of L is in line with that of the Na⁺ complexes, except for the II and V systems. For a given L, the β_1^{NB} -values of Li⁺ complexes

Table 1 Stability constants of 1:1 complexes of Li⁺ and Na⁺ with several acyclic carriers containing 8-quinolyloxy units in water-saturated NB, and the selectivity coefficients for Li⁺ over Na⁺ at 25°C

L	$\log \beta_1^{NB}(\text{Li})^a$	$\log \beta_1^{NB}(\text{Na})^a$	$\log k_{\text{LiNa}}^{\text{pot}}$
I ^b	6.4	4.4	−1.3 (−1.5) ^c
II ^b	6.5	4.2	−1.6 (−1.6) ^c
III ^b	7.2	5.3	−1.2 (−1.1) ^c
IV	7.43±0.06 ^d	5.66±0.06 ^d	−1.1 (−0.98) ^c
V	5.71±0.05 ^d	4.54±0.04 ^d	−0.5 (−0.57) ^c
VI	4.58±0.09 ^d	3.90±0.06 ^d	0.0 (−0.18) ^c
Without carrier	—	—	+0.70(+0.89) ^c

a. $\beta_1^{NB}(M)/\text{mol}^{-1} \text{ dm}^3$.

b. Ref. 4a.

c. Values determined by potentiometry for the PVC-NPOE membrane electrodes. See Ref. 3.

d. Standard deviation.

are larger than the corresponding values of Na⁺ complexes. From this result, we can see that carriers I–VI possess a high coordination ability for Li⁺ over Na⁺.

According to an X-ray diffraction analysis⁷, a crystal of the complex of LiClO₄ with IV has a five-coordinate structure with an *N,N,O,O*-tetradentate IV and a donor oxygen atom of ClO₄[−]. This result suggests that, in the NB-phase, I–VI give complexes with a coordination of *N,N,O,O*-tetradentate carriers in reacting with Li⁺.

The Li⁺-IV complex has the highest stability among the complexes of I–IV and VI containing the bis(8-quinolyloxy)propane units in their molecules. Since the skeleton of IV may be the most flexible in I–IV and VI, the four donor atoms of IV can occupy the optimal position in coordinating with Li⁺. As can be seen from Table 1, the β_1^{NB} -value of the Li⁺-IV complex is much larger than that of the Li⁺-V complex. Furthermore, this value is close to that of 10^{7.0} mol^{−1} dm³ for the Li(DBz14C4)⁺ complex^{4a}, in which Li⁺ fits well into the cavity of the 14C4 ring.^{8,9} In explaining these observations, we point out that in the Li⁺ complexes IV as a ligand can form a four-coordinate structure in a manner similar to that of the *O,O,O,O*-tetradentate 14C4, while V cannot form such a structure because of interference due to the butylene chain connecting the two 8-quinolyloxy units.

The β_1^{NB} -value of the Li⁺-VI complex is much smaller than that of the Li⁺-I complex (Table 1). In the Li⁺-VI complex, the steric hindrance between the methyl groups on the two quinolyloxy units prevents the carrier from forming a four-coordinate structure in a manner similar to that of the tetradentate 14C4. Due to this steric hindrance, the Li⁺-N bonds in the VI complex may be greatly weakened.

A similar discussion holds for the Na⁺ complexes with carriers I, IV, V and VI.

We reported previously that the following equation can be used for calculating the potentiometric selectivity coefficients ($k_{\text{LiNa}}^{\text{pot}}$) of ISEs containing neutral carriers:⁴

$$\log k_{\text{LiNa}}^{\text{pot}} = \log(K_{\text{D,Na}}/K_{\text{D,Li}}) + \log[\beta_1^{\text{NB}}(\text{Na})/\beta_1^{\text{NB}}(\text{Li})], \quad (1)$$

where $K_{\text{D,M}}$ ($\text{M}=\text{Li}, \text{Na}$) denotes the distribution constant ($c_{\text{M}}^{\text{NB}}/c_{\text{M}}$) of the simple metal ion between the w- and the NB-phases at the interfacial potential of 0 V vs. TPh(As/B)E, and is related to $\Delta\phi_{\text{M}}^{\text{oc}}$ as follows: $\Delta\phi_{\text{M}}^{\text{oc}} = -(2.3RT/zF)\log K_{\text{D,M}}$.^{4b,c} The value of $\log(K_{\text{D,Na}}/K_{\text{D,Li}})$ is +0.70;^{4b,c} this positive value means that in the absence of L, Na^+ transfers across the w/NB-interface more easily than does Li^+ . We can calculate the $\log k_{\text{LiNa}}^{\text{pot}}$ -values from the $\log \beta_1^{\text{NB}}$ -values using Eq. (1). As can be seen from the negative values of $\log k_{\text{LiNa}}^{\text{pot}}$ (summarized in Table 1), carriers I–VI in the NB-phase preferably facilitate the transfer of Li^+ across the w/NB-interface compared with that of Na^+ . Their facilitation effect is in the order $\text{VI} < \text{V} < \text{IV} < \text{III} < \text{I} < \text{II}$. This order is in accord with that of the Li^+ selectivity determined potentiometrically for the poly(vinyl chloride)-*o*-nitrophenyl octyl ether (PVC-NPOE) membrane ISEs.³

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