Notes

Ion-Transfer Polarographic Study on the Sodium-Ion Selectivity of Bis(12-crown-4) at a Water/Nitrobenzene Solution Interface

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Liquid membrane ion-selective electrodes (ISEs) based on various synthetic neutral carriers have been developed to obtain high ion selectivity to a given primary ion, such as alkali and alkaline earth metal ions.^{1,2} For example, ISEs containing bis[(12-crown-4)methyl]-2-dodecyl-2-methylmalonate (bis(12C4)) and bis[(benzo-15-crown-5)-4-methyl]pimelate as the carriers (L) possess high Na⁺ and K⁺ selectivity, respectively.^{1a,b} Their ion-selective properties have been estimated potentiometrically by using the Nicolsky–Eisenman equation, and have been expressed as potentiometric selectivity coefficients ($k_{MM'}^{\text{pot}}$) for the primary ion (M) over an interfering ion (M').²

We have recently shown by using ion-transfer polarography that the $k_{MM'}^{\text{pot}}$ -value can be calculated based on the difference in the formal potentials of the following facilitated ion-transfer process across a water(w)/organic(o) solvent interface:³

where i^+ and $i\text{L}^+$ ($i=\text{M}$ and M') denote a univalent metal ion and the corresponding L-complexed ion, respectively. Process (1) consists of two constituent equilibria: (1a) the distribution of the simple metal ion between the w- and the o-phase, $i^+(\text{w-phase}) \rightleftharpoons i^+(\text{o-phase})$, and (1b) the complex formation of the metal ion with L in the o-phase, $i^+(\text{o-phase}) + \text{L(o-phase)} \rightleftharpoons i\text{L}^+(\text{o-phase})$. However, it is not clear which of the two constituent equilibria (1a or 1b) enhances the Na⁺ selectivity of bis(12C4) against interfering ions, such as Li⁺ and K⁺.

In this paper we show that the Na⁺ selectivity of bis(12C4) against Li⁺ or K⁺ can be explained in terms of both the stability constants of their complexed ions in a nitrobenzene (NB) phase and the distribution constants of the simple metal ions between the w- and the NB-phase. Furthermore, it is suggested that the 1:1 complex of Na⁺ with bis(12C4) has a sandwich-type structure.

Experimental

Chemicals

Nitrobenzene and tetrabutylammonium tetraphenylborate (TBA·TPB) were prepared by the same methods as described elsewhere.³ Commercial bis(12C4) (Dojindo Laboratories) was used without further purification. Commercially available 12-crown-4 (12C4, Wako) was purified by vacuum distillation. All other chemicals were of analytical grade and were used without further purification. The concentrations of LiCl, NaCl, KCl and the carriers employed were determined using a previously reported procedure.³

Electrochemical measurements

The temperature of the electrochemical cell was controlled at 25.0±0.5°C with a thermostated water bath. The galvanic cell employed for controlling the measurements of the potential difference at the w/NB-interface was as follows:

where the test interface is between phase II and III, and c_{M} and c_{L}^{NB} denote the bulk concentration of the metal ion in the w-phase and that of the carrier L in the NB-phase, respectively. For the NaCl-bis(12C4) system, we reduced the concentration of NaCl in the w-phase III to less than 10⁻¹ mol dm⁻³, because the facilitation effect of bis(12C4) on Na⁺ transfer across the w/NB-interface was

very large. Hence, $0.1 \text{ mol dm}^{-3} \text{ MgSO}_4$ was added to phase III as a supporting electrolyte. The values of the potentials ($\Delta\phi$) were standardized on the basis of the extrathermodynamic assumption described before^{3a} and are designated as V vs. TPh(As/B)E , which is the abbreviated form of a tetraphenylarsonium tetraphenylborate electrode. The other procedure and experimental conditions were the same as in previous papers.³

Results and Discussion

Well-defined facilitated waves were observed at potentials 40–150 mV more negative than the final rise, except for the LiCl- and KCl-12C4 systems, for which we could not separate the facilitated waves from the final rise. Figure 1 shows a typical polarogram for the NaCl-bis(12C4) system. Logarithmic plots of the current-potential curves yielded straight lines with reciprocal slopes of $60 \pm 1 \text{ mV/decade}$ for the LiCl-bis(12C4) system, 60 ± 1 for NaCl-bis(12C4), 59 ± 1 for KCl-bis(12C4) and 60 ± 1 for NaCl-12C4. The values of the reciprocal slopes indicate that the univalent complexes transfer across the w/NB-interface and the facilitated waves are reversible. Figure 2 represents the half-wave potentials ($\Delta\phi_{1/2}$) of the bis(12C4) complexes against $\log c_M$ ($M=\text{Li, Na and K}$). For a comparison, the same plot for the NaCl-12C4 system is also shown in Fig. 2. For all cases, we obtained straight lines with slopes of about -59 mV/decade , indicating that only 1:1 complexes were formed in the NB-phase.³

As previously described³, we can evaluate the stability constants ($\beta_1^{\text{NB}}/\text{mol}^{-1} \text{ dm}^3$) of the 1:1 complexes in the water-saturated NB-phase from plots of the F_A function, defined by $F_A = \exp[(zF/RT)(\Delta\phi_{1/2} - \Delta\phi_M^0)]$, against $1/c_M$. The obtained results are summarized in Table 1. As can be seen from Table 1, the sequence of the $\log \beta_1^{\text{NB}}$ -values is $M=\text{Na} \gg \text{Li} > \text{K}$ for the bis(12C4) complexes and $\text{Na} > \text{K} \approx \text{Li}$ for the 12C4 complexes.⁴ The stability

Fig. 1 Polarograms of $0.0121 \text{ mol dm}^{-3} \text{ NaCl}$ in the absence (curve 1) and presence (curve 2) of bis(12C4) in the NB-phase. $c_{\text{bis(12C4)}}^{\text{NB}} = 0.76 \text{ mmol dm}^{-3}$. The reciprocal slope $= 0.061 \text{ V}$; the half-wave potential $= -0.055 \text{ V}$.

Fig. 2 Half-wave potentials of the bis(12C4) and 12C4 complexes against $\log c_M$ ($M=\text{Li, Na and K}$). L: bis(12C4) (open symbols); 12C4 (full circle). The slopes of the straight lines were -55 mV/decade ($M=\text{Li}$), -64 (Na) and -54 (K) for the bis(12C4) systems and -57 (Na) for the 12C4 system.

Table 1 Stability constants of 1:1 complexes with LiCl, NaCl and KCl in the water-saturated NB-phase and their Na^+ selectivity coefficients at 25°C

MCl-L	$\log \beta_1^{\text{NB}}$	$\log k_{\text{NaM}}^{\text{pot}}$
LiCl-bis(12C4)	5.7 ₀	-3.8 (-3) ^a
NaCl-	8.8 ₂	—
KCl-	5.4 ₂	-1.5 (-2) ^a
LiCl-12C4	$\leq 4^b$	≤ -3
NaCl-	6.4 ₉	—
KCl-	$\leq 5^b$	$\leq 0.4 (-0.2)^a$

a. Values obtained by potentiometry for the poly(vinyl chloride)-*o*-nitrophenyl octyl ether (PVC-NPOE) membrane electrode. See refs. 1a), 1b) and 2.

b. Ref. 4.

constant of the Na^+ -bis(12C4) complex is larger than that of the Na^+ -12C4 complex by a factor of about 200. This observation suggests that Na^+ interacts with the two 12C4 units in bis(12C4) to form the 1:1 complex, which has the intramolecular sandwich-type structure.⁵ This may be supported by the fact that the β_2^{NB} -value ($\text{mol}^{-2} \text{ dm}^6$) of the sandwich-type 1:2 (M to L) complex of Cs^+ with dibenzo-18-crown-6 (DB18C6) is about 200-times as large as the β_1^{NB} -value of the 1:1 complex; $\log \beta_1^{\text{NB}} = 3.1$ and $\log \beta_2^{\text{NB}} = 5.4$.^{3a,6} A similar result was reported for the case of the 1:1 and 1:2 barium(II) complexes of DB18C6.⁷

The $\log \beta_1^{\text{NB}}$ -value of the Li^+ -bis(12C4) complex is also larger than that of the Li^+ -12C4 complex, although the

difference between the stability constants of the Li^+ complexes of bis(12C4) and 12C4 is smaller than the difference for their Na^+ complexes. This fact suggests that the Li^+ complex has a structure that is similar to that of the Na^+ -bis(12C4) complex.

According to the previous results^{3b,c,8}, the potentiometric selectivity coefficients of the neutral carrier-type ISEs can be expressed as

$$\log k_{\text{MM}'}^{\text{pot}} = \log(K_{\text{D,M}'} / K_{\text{D,M}}) + \log[\beta_1^{\text{NB}}(\text{M}') / \beta_1^{\text{NB}}(\text{M})], \quad (2)$$

where $K_{\text{D},i} = c_i^{\text{NB}} / c_i$ ($i = \text{M}$ and M') at the interfacial potential of 0 V vs. TPh(As/B)E, and is related to the ion-transfer formal potential ($\Delta\phi_i^\circ$) as $\Delta\phi_i^\circ = -(2.3RT/zF) \times \log K_{\text{D},i}$. The first term on the right hand side of Eq. (2) corresponds to the difference between the transfer (or distribution) ability of the simple metal ions across the w/NB-interface; thus, this term becomes constant regardless of the kinds of L. The values of the term $\log(K_{\text{D,M}'} / K_{\text{D,Na}})$ are -0.70 for $\text{M}' = \text{Li}$ and $+1.89$ for $\text{M}' = \text{K}$.^{3c} Table 1 lists the Na^+ selectivity coefficients of bis(12C4) and 12C4 against Li^+ and K^+ , which were calculated using Eq. (2). The $\log k_{\text{NaM}'}^{\text{pot}}$ -values ($\text{M}' = \text{Li}$ and K) obtained polarographically are in agreement with their literature values² obtained potentiometrically by using ISE.

As can be seen from Table 1, bis(12C4) has the high selectivity for Na^+ over K^+ though Na^+ is lower than K^+ for the transfer ability of the simple ion at the w/NB-interface. This finding indicates that this high Na^+ selectivity of bis(12C4) against K^+ is due to a large difference between the stability constants of the Na^+ - and K^+ -bis(12C4) complexes in the NB-phase. On the other hand, the much higher Na^+ selectivity of bis(12C4) against Li^+ is caused by the large difference between the values of β_1^{NB} and $K_{\text{D},i}$ for the Na^+ -bis(12C4) system and those for the Li^+ -bis(12C4) system.

To characterize the high Na^+ selectivity of bis(12C4), it is interesting to compare the $\log k_{\text{NaM}'}^{\text{pot}}$ -values of the bis(12C4) complexes with those of the 12C4 complexes. The $\log k_{\text{NaLi}}^{\text{pot}}$ -value of bis(12C4) is nearly equal to that of 12C4, while the $\log k_{\text{NaK}}^{\text{pot}}$ value of bis(12C4) is much smaller than that of 12C4. Considering the difference between the β_1^{NB} -values of the 12C4 and bis(12C4) complexes, this fact means that the enhancement of the β_1^{NB} -values due to the modification of L does not necessarily improve the selectivity of L for the primary ion, since such a modification may cause an enhancement of the β_1^{NB} -values for both the primary and interfering ions.

In conclusion, Eq. (2) is an effective expression for the ion selectivity of the present neutral carriers, as described in previous papers.^{3b,c} This result also suggests that the ion selectivity of L at the w/o-interface, which can be determined by the ion-transfer polarography, mainly governs the ion selectivity estimated for ISE, especially the liquid membrane-type ISE.

References and Notes

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4. The facilitation effect of 12C4 on Li^+ and K^+ were very small. Hence, the minimum β_1^{NB} -values, which we can determine experimentally, are in the range of $10^4 - 10^5 \text{ mol}^{-1} \text{ dm}^3$, because, with the galvanic cell employed in the present work, the positive final rises appear around +200 mV for Li^+ and around +140 mV for K^+ . From the above facts, it can be concluded that the logarithmic β_1^{NB} -values are equal to or less than 4 for the Li^+ complex of 12C4 and 5 for its K^+ complex.
5. For example, K. H. Wong, M. Bourgoin and J. Smid, *J. Chem. Soc., Chem. Commun.*, **1974**, 715.
6. Hydrophilic 12-crown-4 dissolves easily from the NB-phase into the w-phase under the condition of $c_{12\text{C}4}^{\text{NB}} \gg c_{\text{Na}}$, so that we can not determine accurate half-wave potentials, because no well-defined polarograms for the 1:2 complex of Na^+ with 12C4 are obtained. Practically, we can not determine the β_2^{NB} -value of its complex by using the present method.
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