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Ion-transfer Polarographic Study of the Distribution of Alkali and Alkaline-Earth Metal Complexes with 3*m*-Crown-*m* Ether Derivatives (m = 6, 8) between Water and Nitrobenzene Phases

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Abstract. Stability constants (β_1^{NB}) of the 1 : 1 cationic complexes of Li^+, Na^+, K^+, Ca^{2+}, Sr^{2+} and Ba^{2+} with benzo-18-crown-6 (B18C6), Ca^{2+} and Sr^{2+} with 18C6 and dibenzo-18C6 and Li^+, Na^+, Ca^{2+}, Sr^{2+} and Ba^{2+} with dibenzo-24-crown-8 in a nitrobenzene (NB) solution saturated with water (w) were determined at 25 °C by ion-transfer polarography. From these values, distribution constants ($K_{\mathrm{D,ML}}$) of the 18C6-derivative complex cations between the w- and NB-phases were evaluated using the thermodynamic relation: $K_{\mathrm{D,ML}} = K\beta_1^{\mathrm{NB}}$, where K (mol dm^{-3}) is an overall equilibrium constant of the processes related to the complexation in the w-phase. The data on the distribution of the 18C6-derivative complex cations between the two phases and the complexation in the NB-phase were examined on the basis of an increase in the number of water molecules hydrated to the species relevant to these processes. The 18C6 derivatives showed higher solubilities in the NB-phase than in the w-phase by complexing with the univalent-metal ions, while, for the divalent-metal ions, the derivatives showed lower solubilities in the NB-phase.

Key words: Distribution constant, stability constant, crown ether complexes, nitrobenzene, ion-transfer polarography.

1. Introduction

Many crown ether derivatives have been used as neutral carriers in liquid membranes for ion transport experiments and ion-selective electrodes (ISEs) [1,2]. Most of the transport experiments are carried out by using polar organic solvents, such as 1,2-dichloroethane and nitrobenzene (NB), as liquid membranes. Also, ISEs contain NB and its derivatives as plasticizers or membrane solvents [2]. In these polar solvents, metal complexes of the crown ethers are present as highly-dissociated complex cations [3]. Therefore, in order to investigate the transfer of these cations across a water (w)/membrane interface, we require their individual distribution

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constants. For alkali metal ions, Makrlik *et al.* [4] and the present authors [5] have reported the distribution constants of the complexes of these cations with dibenzo-18-crown-6 (DB18C6) and 15-crown-5 derivatives, respectively, between the w- and NB-phases. However, the distribution of the complex cations with various crown ethers has not been studied systematically. Moreover, few studies of the distribution of the divalent-metal complex cations into the NB-phase have been reported so far [5], due to the lack of data on stability constants of the divalent complex cations in the NB-phase [6].

In the present paper we have used ion-transfer polarography [7] to determine the stability constants (β_1^{NB}) of the 1 : 1 cationic complexes of alkali (Li–K) and alkaline-earth metal (Ca–Ba) ions with benzo-18-crown-6 (B18C6), Ca^{2+} and Sr^{2+} with 18C6 and DB18C6 and Li^+, Na^+, Ca^{2+}, Sr^{2+} and Ba^{2+} with dibenzo-24-crown-8 (DB24C8) in the NB solution saturated with water at 25 °C. From these values, the distribution constants of the 18C6-derivative complex cations between the w- and NB-phases were evaluated by using the thermodynamic cycle related to the complexation in the NB- and w-phases. Based on these results, we discuss the effect of the hydration water on the complexation processes in the NB-phase and on the distribution of the 18C6-derivative complex cations.

2. Experimental

2.1. CHEMICALS

Commercial 18C6 (Nisso Co Ltd.) and DB18C6 (Nisso) were recrystallized from acetonitrile and benzene, respectively, and then dried *in vacuo*. Benzo-18-crown-6 (Tokyo Chemical Industry Co Ltd.) and DB24C8 (Merck) were dried *in vacuo* before use. Tetrabutylammonium tetraphenylborate (TBA^+TPB^-) was prepared by the method described previously [8]. Nitrobenzene was purified by the method reported by Osakai *et al.* [9]. All other chemicals were of analytical grade and were used without further purification.

Four-times-distilled water was used to prepare aqueous electrolyte solutions. The molar concentrations of the aqueous solutions of alkali metal chlorides were determined by precipitation analysis. Also, the concentrations of the aqueous solutions of alkaline-earth metal chlorides were determined by both precipitation analysis and EDTA titration. These standard solutions were used for the ion-transfer polarographic measurements by diluting to the concentrations of 0.04–0.9 mol dm^{-3} for Li^+, 0.04–0.5 for Na^+, 0.004–0.05 for K^+, 0.03–0.6 for Ca^{2+}, 0.03–0.6 for Sr^{2+} and 0.03–0.5 for Ba^{2+}. The NB-phases of the crown ethers (0.2–0.7 mmol dm^{-3}) were prepared by direct weighing. The NB- and w-phases were saturated with water and NB, respectively, at 25 °C before use.

2.2. ELECTROCHEMICAL MEASUREMENTS

The galvanic cell employed for controlling or measuring the potential difference ($\Delta\phi$) at the w/NB interface was as follows:

(RE1) Ag | AgCl | 0.05 mol dm^{-3} TBA^+Cl^- (phase w) |
0.05 mol dm^{-3} TBA^+TPB^- + $[L]^{NB}$ L (NB) |* [M] $M^{Z+}(Cl^-)_Z$ (w) |
sat. KCl (w) | 0.05 mol dm^{-3} KCl (w) | AgCl | Ag (RE2).

Here, the test interface is marked by an asterisk and [M] and $[L]^{NB}$ denote the initial concentration of the metal (M) ion in the w-phase and that of the crown ether (L) in the NB-phase, respectively: z is the electric charge of M. The temperature of the cell was controlled at 25.0 ± 0.5 °C by using a thermostatted water bath.

Polarographic maxima were observed for the Na^+– and K^+–B18C6 systems. Hence we suppressed these maxima by adding 0.3 to 0.7 mmol dm^{-3} sorbitan monooleate (Nacalai Tesque Co Ltd.) to the NB-phase [10]. For the same reason as given earlier [10], 0.1 mol dm^{-3} $MgSO_4$, as the supporting electrolyte, was added to the w-phase of $M^{Z+}(Cl^-)_Z$ for the K^+–B18C6 system.

The values of $\Delta\phi$ obtained in this study were standardized on the basis of the 'extrathermodynamic or $Ph_4As^+BPh_4^-$ assumption' as described by Rais [11], and designated as V vs. TPh(As/B)E (the $Ph_4As^+BPh_4^-$ electrode).

3. Results

Well defined facilitated waves were observed at potentials sufficiently more negative than the final rise (Figure 1). Log-plot analysis of these facilitated waves yielded straight lines with reciprocal slopes (number of runs given in parentheses) of 60 ± 1 mV/decade (13) for the Li^+–B18C6 system, 59 ± 2 (9) for Na^+–B18C6, 57 ± 2 (14) for K^+–B18C6, 58 ± 1 (9) for Li^+–DB24C8, 59 ± 1 (8) for Na^+–DB24C8, 33 (3) for Ca^{2+}–18C6, 30 (4) for Sr^{2+}–18C6, 33 ± 2 (10) for Ca^{2+}–B18C6, 34 ± 1 (9) for Sr^{2+}–B18C6, 33 ± 1 (9) for Ba^{2+}–B18C6, 31 ± 1 (6) for Ca^{2+}–DB18C6, 32 ± 2 (12) for Sr^{2+}–DB18C6, 32 ± 1 (10) for Ca^{2+}–DB24C8, 33 ± 1 (8) for Sr^{2+}–DB24C8 and 30 ± 1 (9) for Ba^{2+}–DB24C8. Limiting currents were verified to be diffusion-controlled with respect to $[L]^{NB}$. These results indicate that the facilitated waves observed in this study correspond to the reversible transfer of univalent and divalent cations across the w/NB interface [8].

Half-wave potentials ($\Delta\phi_{1/2}$), obtained from the log-plot analysis, are plotted against log[M] for M = Li, Na, K, Ca, Sr and Ba. Figures 2 and 3 show typical plots of $\Delta\phi_{1/2}$ vs. log[M] for M^{Z+}–L systems. According to our previous paper [8], $\Delta\phi_{1/2}$ measured under the condition of $[M] \gg [L]^{NB}$ is expressed as follows:

$$\begin{aligned}\Delta\phi_{1/2} &= \Delta\phi_M^{0\prime} - (RT/zF)\ln\xi + (RT/zF) \\ &\quad \times \ln\{(1 + \xi K_{D,L} + \beta_1^{w}[M])/K_{D,L}\beta_1^{NB}[M]\}, \qquad (1)\end{aligned}$$

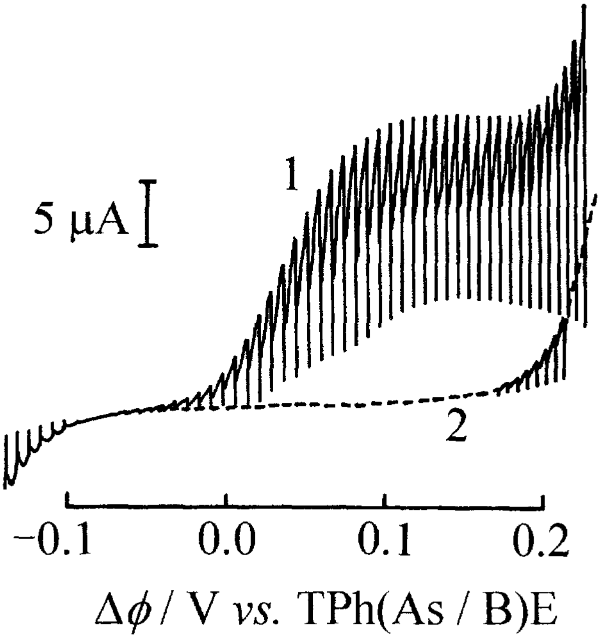

Figure 1. Polarograms of 0.0314 mol dm^{-3} BaCl$_2$ in the presence (curve 1) and absence (curve 2) of B18C6 in the NB-phase. [B18C6]$^{\mathrm{NB}}$ = 0.320 mmol dm^{-3}. The reciprocal slope = 0.034 V; the half-wave potential = 0.037 V.

where $\Delta\phi^{0\prime}_{\mathrm{M}}$, ξ, $K_{\mathrm{D,L}}$ and β_1^{x} denote the ion-transfer formal potentials, at $\Delta\phi = 0$ V vs. TPh(As/B)E, of M^{Z+} across the w/NB interface, the square root of the ratio of diffusion coefficients, the distribution constant of L between the w- and NB-phases and the stability constant of the 1 : 1 complex in the x-phase (x = w, NB), respectively. In order to obtain the values of β_1^{NB} and β_1^{w} from the concentration dependence of $\Delta\phi_{1/2}$ given by Equation (1), the equation has been rearranged in the following form [8]

$$\begin{aligned} F_{\mathrm{A}} &\equiv \exp[(zF/RT)(\Delta\phi_{1/2} - \Delta\phi^{0\prime}_{\mathrm{M}})] \\ &= (\beta_1^{\mathrm{w}}/\xi K_{\mathrm{D,L}}\beta_1^{\mathrm{NB}}) + \{(1+\xi K_{\mathrm{D,L}})/\xi K_{\mathrm{D,L}}\beta_1^{\mathrm{NB}}\}[\mathrm{M}]^{-1}. \end{aligned} \tag{2}$$

When F_{A} is plotted against [M]$^{-1}$ as shown in Figure 4, a straight line is obtained with an intercept $\beta_1^{\mathrm{w}}/\xi K_{\mathrm{D,L}}\beta_1^{\mathrm{NB}}$ and a slope $(1+\xi K_{\mathrm{D,L}})/\xi K_{\mathrm{D,L}}\beta_1^{\mathrm{NB}}$. Hence we can obtain the values of β_1^{NB} and β_1^{w} from the slope and intercept by using the ξ and $K_{\mathrm{D,L}}$ values reported previously [8]. The logarithmic β_1^{NB} values thus obtained are summarized in Table I, together with other β_1^{NB} values available from the literature. In particular, when the $K_{\mathrm{D,L}}$ values are very large, the straight line passes through the origin, within experimental error, so that the β_1^{w} values cannot be obtained from the intercept. In some cases, however, the β_1^{w} values are obtained from the

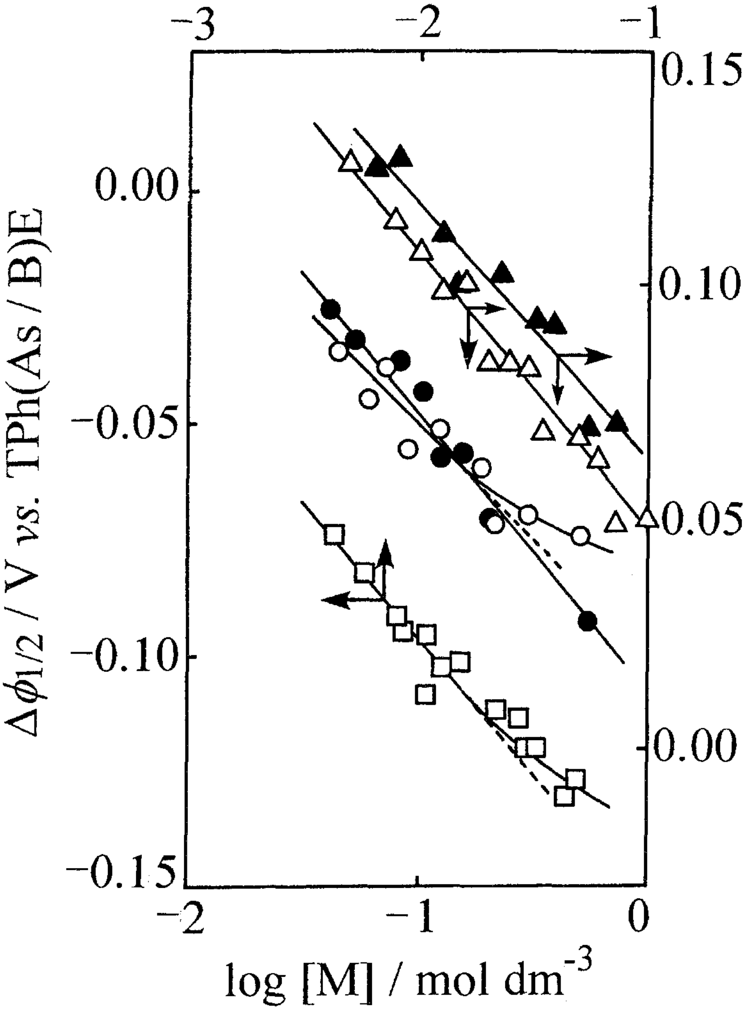

Figure 2. Half-wave potentials $\Delta\phi_{1/2}$ of M^+–L complexes against log[M]. Li^+–B18C6 (Δ), Na^+–B18C6 (○), K^+–B18C6 (□), Li^+–DB24C8 (▲) and Na^+–DB24C8 (●) complexes.

intercept. Fortunately, the β_1^w values for the Na^+– and K^+–B18C6 systems could be determined. The log β_1^w values of $Na(B18C6)^+$ and $K(B18C6)^+$ complexes are 1.8 and 2.0, respectively. These values are 0.2–0.5 units greater than those obtained previously by potentiometry with ISEs [12].

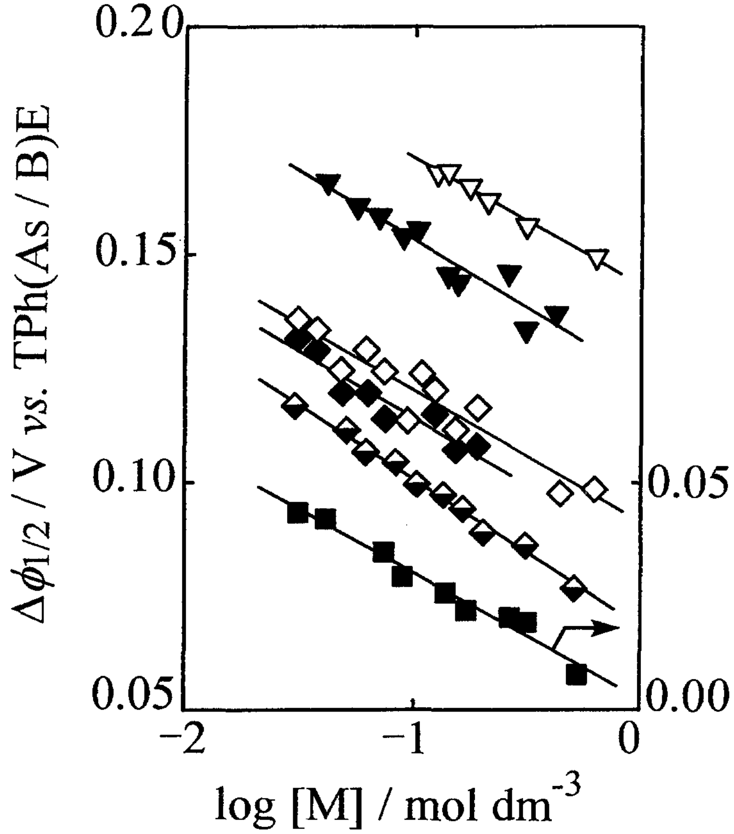

Figure 3. Half-wave potentials $\Delta\phi_{1/2}$ of M^{2+}–L complexes against log[M]. Ca^{2+}–B18C6 (◈), Ca^{2+}–DB18C6 (▽), Sr^{2+}–DB18C6 (◇), Ca^{2+}–DB24C8 (▼), Sr^{2+}–DB24C8 (◆) and Ba^{2+}–DB24C8 (■) complexes.

4. Discussion

4.1. COMPLEXATION IN THE NB SOLUTION SATURATED WITH WATER

Previously, we have expressed the complexation of M^{Z+} with L in the NB solution saturated with water by the following stoichiometric equation [5,13]:

$$M^{Z+}(H_2O)_k + L(H_2O)_l \rightleftharpoons ML^{Z+}(H_2O)_n + (k + l - n)H_2O, \qquad (3)$$

where k, l and n refer to the numbers of water molecules attached to a metal ion, a crown ether and a complex, respectively. Iwachido *et al.* [3] have determined these values by Karl–Fischer titration and then made clear the effect of the crown ethers on the cation hydration in the solvent extraction into the NB-phase. Now, defining f_w as

$$f_w \equiv n/(k + l) \qquad (4)$$

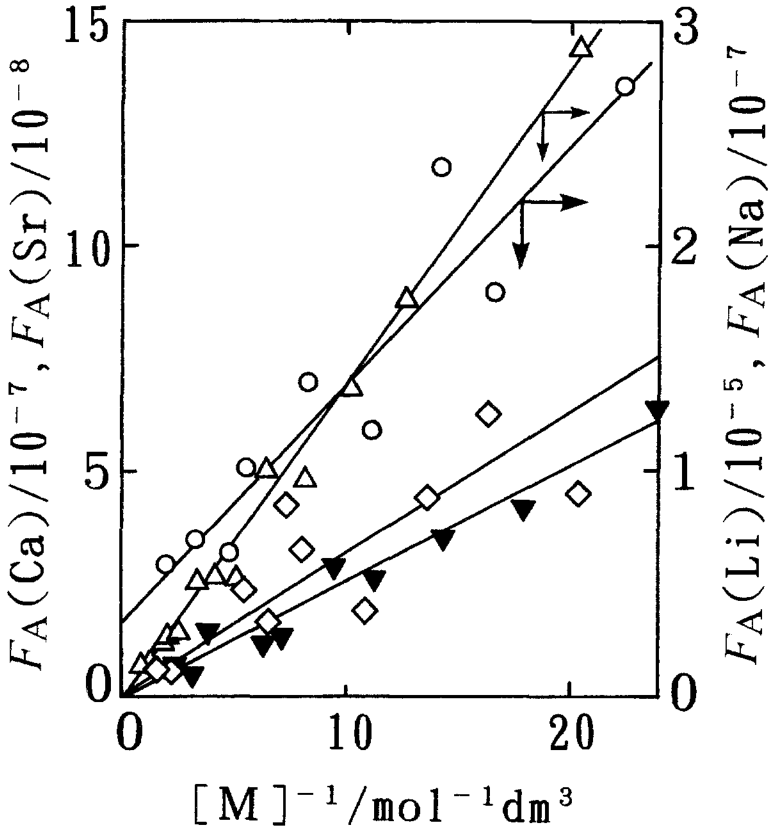

Figure 4. Plots of F_A vs. $[M]^{-1}$ for the Li^+–B18C6 (△), Na^+–B18C6 (○), Sr^{2+}-DB18C6 (◇) and Ca^{2+}-DB24C8 (▼) systems.

based on Equation (3), this value expresses the fraction of stoichiometric water formally associated with the complex and can reflect the strength of the binding between water molecules and M^{Z+} held in the cavities in complexation with the ligands in the NB solution. From the k, l and n values, we can calculate the f_w values. For example, introducing $k = 5.6$, $l = 1.6$ and $n = 2.5$ (see Table II) into Equation (4), one then obtains 0.35 for the Li(18C6)$^+$ system. Table I lists the f_w values thus calculated.

For any L, the log β_1^{NB} values of the univalent-metal complexes increase with a decrease in their f_w values (Table I). The f_w values of the 18C6-derivative complexes suggest a larger shielding effect of these derivatives on K^+ held in the cavities than on Li^+ and Na^+. The f_w values of the K^+ complexes with the 18C6 derivatives are very small. This fact means that the coordination number of K^+ is almost satisfied by binding with only the donor oxygen atoms of the 18C6 derivatives. Similar explanations can hold also for K(DB24C8)$^+$ and Na(DB24C8)$^+$.

Table I. Stability constants of alkali and alkaline-earth metal complexes with several crown ethers in the NB solution saturated with water at 25 °C

L	$\log\beta_1^{NB}$, f_w ( )[a]					
M =	Li	Na	K	Ca	Sr	Ba
18C6	7.5[b]	8.5[b]	9.3[b]	11.2	13.1	13.4[b]
	(0.35)	(0.24)	(0.10)	(0.32)	(0.34)	(0.28)
B18C6	5.87	7.91	7.72	9.43	11.1	11.6
	(0.41)	(0.26)	(0.19)	(0.40)	(0.36)	(0.37)
DB18C6	4.8[c]	6.8[b]	6.9[b]	7.00	8.51	8.8[b]
	4.5[d]			(0.38)	(0.38)	(0.40)
	(0.47)	(0.29)	(0.05)			
DB24C8	5.67	7.80	6.6[c]	7.59	8.64	11.1
	5.5[c]	7.7[c]		(0.39)	(0.32)	(0.26)
	(0.39)	(0.05)	(0.17)			

[a] f_w values calculated from Equation (4).
[b] Refs. 8 and 10.
[c] See, Z. Samec and P. Papoff: *Anal. Chem.* **62**, 1010 (1990).
[d] At 22 ± 1 °C. Ref. 4.

Table II. Distribution constants of the ML^{z+} complexes between the w- and NB-phases at 25 °C

L	$\log K_{D,L}$ [a]	$\log K_{D,ML}$,[b] $h(j)$ [ ][c]					
	M =	Li	Na	K	Ca	Sr	Ba
18C6	−1.0	−0.2	0.7[d]	2.2	−2.1	−2.2	−2.6[d]
	[1.6]	[2.5]	[1.2]	[0.3]	[4.7]	[4.6]	[3.4]
B18C6	1.57	–	2.1	3.4	−1.3	−1.3	−0.8
	[0.8]	[2.6]	[1.1]	[0.4]	[5.5]	[4.6]	[4.2]
DB18C6	4.4	–	4.1[d]	5.5	>−0.4	0.3	0.2[d]
	[0.6]		4.3[e]	5.3[d]	[5.1]	[4.9]	[4.4]
				5.5[e]			
		[2.9]	[1.2]	[0.1]			
Without L[f]		−6.68	−5.98	−4.09	−11.8	−11.6	−11.1
		[5.6]	[3.5]	[1.3]	[13.0]	[12.1]	[10.5]

[a] Ref. 16.
[b] $\log K_{D,ML} = \log K_{D,L} + \log K_{D,M} + \log\beta_1^{NB} - \log\beta_1^{w}$.
[c] The numbers of water molecules coextracted with M^{z+}, ML^{z+} and L as defined in Equation (3), respectively. Ref. 3.
[d] Ref. 5.
[e] At 22 ± 1 °C. Ref. 4.
[f] $\log K_{D,M}$ values. Refs. 11 and 17.

The $\log\beta_1^{\mathrm{NB}}$ values of the divalent-metal complexes are in the order $\mathrm{CaL}^{2+} < \mathrm{SrL}^{2+} \leq \mathrm{BaL}^{2+}$ for a given L (Table I). Nevertheless, the f_{w} values are nearly the same except for DB24C8. According to X-ray diffraction data for aqua complexes in aqueous electrolyte solutions [14], Sr^{2+} and Ba^{2+} can easily form 8-coordinate complexes. Hence, in the NB solution saturated with 0.178 mol dm^{-3} water (at 25 °C) [3], these metal ions can still form 8-coordinate complexes in which the coordination sites of Sr^{2+} and Ba^{2+} are filled with water molecules in addition to the donor oxygen atoms of L. On the other hand, Ca^{2+} can form a 6-coordinate complex, e.g., $[\mathrm{Ca(OH_2)_6}]^{2+}$ [13], so that the coordination site of Ca^{2+} can be filled with only the donor oxygen atoms of L. This difference can reduce the f_{w} values in the complexation of the 18C6 derivatives with Ca^{2+}, while increasing the f_{w} values for Sr^{2+} or Ba^{2+}. Therefore it can be seen that the f_{w} values in the complexation with Ca^{2+}, Sr^{2+} and Ba^{2+} become nearly the same (Table I). For DB24C8, its larger conformational flexibility and eight donor oxygen atoms may play an important role in the release of water molecules hydrating the divalent-metal ions, in comparison with the 18C6 derivatives, especially DB18C6.

The sequences of $\log\beta_1^{\mathrm{NB}}$ values of the 18C6-derivative complexes are $\mathrm{M(18C6)}^{+} > \mathrm{M(B18C6)}^{+} > \mathrm{M(DB18C6)}^{+}$ for M = Li, Na and K. The sequences of the f_{w} values become the inverse, except for K. These facts show that the shielding effect of the 18C6 derivatives on the central metal ion increases in the order DB18C6 < B18C6 < 18C6, corresponding to that of their conformational flexibility. Similar results were also obtained for the M^{2+}–18C6 derivative complexes.

The crystal ionic radius of K^{+} (1.38 Å) is nearly equal to that of Ba^{2+} (1.36 Å for the 6-coordinate structure and 1.42 for the 8-coordinate one) [15]. The BaL^{2+} complexes in the NB solution are much more stable than the KL^{+} complexes (Table I). The f_{w} values of the BaL^{2+} complexes are much larger than those of the KL^{+} complexes. Similar results were observed also for the L–Na^{+} (ionic radius 1.02 Å [15]) and –Ca^{2+} (1.00 Å [15]) systems. These results allow us to state that the divalent-metal ions bind more strongly with the donor oxygen atoms in both L and H_2O than do the univalent-metal ions in the NB solution.

4.2. DISTRIBUTION OF THE COMPLEX CATIONS

From the thermodynamic cycle of the complexation in the NB- and w-phases and the distribution of M^{Z+}, L and ML^{Z+} between the two phases [4,5], the following relation can be derived:

$$K_{\mathrm{D,ML}} = K_{\mathrm{D,L}}K_{\mathrm{D,M}}\beta_1^{\mathrm{NB}}/\beta_1^{\mathrm{w}} \equiv K\beta_1^{\mathrm{NB}} \tag{5}$$

with

$$K_{\mathrm{D,ML}} \equiv c_{\mathrm{ML}}^{\mathrm{NB}}/c_{\mathrm{ML}} = \exp[(-zF/RT)\Delta\phi_{\mathrm{ML}}^{0\prime}] \tag{6}$$

$$K_{\mathrm{D,M}} \equiv c_{\mathrm{M}}^{\mathrm{NB}}/c_{\mathrm{M}} = \exp[(-zF/RT)\Delta\phi_{\mathrm{M}}^{0\prime}]. \tag{7}$$

Here, c_j^{NB}, c_j, $K_{\mathrm{D,M}}$ and $\Delta\phi_{\mathrm{ML}}^{0\prime}$ denote the concentrations of species j^{Z+} (j = M, ML) at equilibrium in the NB-phase, those in the w-phase, the distribution constant of M^{Z+} between the two phases and the ion-transfer formal potentials at $\Delta\phi = 0$ V of ML^{Z+} across the w/NB interface, respectively. Hence we can calculate the $K_{\mathrm{D,ML}}$ values by Equation (5), since the $K_{\mathrm{D,L}}$ [16], $K_{\mathrm{D,M}}$ [11,17] and $\beta_{\mathrm{I}}^{\mathrm{w}}$ [6,16] values are available from the literature. Table II summarizes the logarithmic $K_{\mathrm{D,ML}}$ values calculated for the 18C6-derivative complexes, together with the corresponding literature values of uncomplexed M^{Z+} and free ligands.

The $\log K_{\mathrm{D,ML}}$ values of the univalent-metal complexes are larger than or nearly equal to the $\log K_{\mathrm{D,L}}$ values. This fact indicates that most ligands employed show higher solubilities in the NB-phase than in the w-phase in complexation with the univalent-metal ions. As can be seen from Table II, the sequences of the $\log K_{\mathrm{D,ML}}$ values are $\mathrm{LiL}^+ < \mathrm{NaL}^+ < \mathrm{KL}^+$ for L = 18C6 and $\mathrm{NaL}^+ < \mathrm{KL}^+$ for B18C6 and DB18C6. According to solvent extraction data reported by Iwachido *et al.* [3], the number, $h(\mathrm{ML})$, of water molecules coextracted with ML^+ into the NB-phase are in the order $\mathrm{LiL}^+ > \mathrm{NaL}^+ > \mathrm{KL}^+$ (Table II). These results show that the solubility of ML^+ in the NB-phase increases with a decrease in the $h(\mathrm{ML})$ values from M = Li to K. This is also true for the relation between the $\log K_{\mathrm{D,M}}$ values of the uncomplexed M^+ and the $h(\mathrm{M})$ values.

The $\log K_{\mathrm{D,ML}}$ values of the divalent-metal complexes are much smaller than the $\log K_{\mathrm{D,L}}$ values. This fact shows that the ligands investigated do not have enough effect to shield the electric charge of the divalent-metal ions in comparison with the univalent-metal ions. The $\log K_{\mathrm{D,ML}}$ values are nearly the same within experimental error, although the $h(\mathrm{ML})$ values decrease slightly from M = Ca to Ba. A similar relation holds for the $\log K_{\mathrm{D,M}}$ values of M^{2+} and the $h(\mathrm{M})$ values.

The $\log K_{\mathrm{D,ML}}$ values are in the order 18C6 < B18C6 < DB18C6 for M=Na, K, Ca, Sr and Ba (Table II). This order is in good agreement with that of the hydrophobicity of the ligands, $\log K_{\mathrm{D,L}}$. In spite of an increase in the $\log K_{\mathrm{D,ML}}$ values from L = 18C6 to DB18C6, the corresponding $h(\mathrm{ML})$ values are nearly the same for a given M^{Z+}. On the other hand, the $h(\mathrm{L})$ values decrease in the order 18C6 > B18C6 ≥ DB18C6, suggesting the presence of hydrogen bonding between the 18C6 derivatives and the water molecules [18,19]. These facts show that most water molecules coextracted with ML^{Z+} do not directly interact with L but with M^{Z+} held in the cavity of L [3]. From the results, it is suggested that, in the w-phase, interactions between the ML^{Z+} cations and the water molecules, based on ion-dipole force and hydrogen bonding, decrease in the order 18C6 > B18C6 > DB18C6.

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