Evaluation of the Hydrophilic Property of Sodium Ion-pair Complexes with 3*m*-Crown-*m* Ethers (*m* = 5, 6) and Their Benzo-derivatives by Solvent Extraction

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The ion-pair formation constants $\{K_j^0; j = \text{MA (metal salt), MLA}\}$ of NaO_2CCF_3 (Na^+tfa^-) and its ion-pair complexes (MLA) in water (w) were determined potentiometrically at 25°C and an ionic strength (*I*) of zero. 15-Crown-5 (15C5), 18-crown-6 ethers (18C6), and their mono-benzo derivatives were used as crown ethers (L). The extraction of Natfa by these four L from w into 1,2-dichloroethane was done at 25°C, and then the extraction constants (K_{ex}) for NaLtfa were calculated by using the K_j values, which were estimated from the corresponding K_j^0 ones at *I* of the w-phases, and other equilibrium constants. Also, the distribution constants ($K_{\text{D,MLA}}$) of NaLtfa between the two phases were obtained from a thermodynamic cycle expressing K_{ex} . An interaction of w-molecules with NaLA was considered using a relation of $\log K_{\text{D,MLA}}$ with $\log K_{\text{D,L}}$, derived from the Scatchard-Hildebrand equation, where $K_{\text{D,L}}$ denotes the distribution constant of L between the two phases. The interaction increased in the order of NaL (picrate) < free L ≤ NaLMO₄ (M = Mn, Re) < NaLtfa for L = 15C5 and 18C6.

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Introduction

It has been known that crown ethers (L) extract univalent metal ions (M^+) into less-polar organic (o) phases by an ion-pair extraction with the formation of ion-pair complexes (MLA: $\text{A}^- =$ a pairing anion) in water (w) phases.^{1,2} In the course of such extraction studies, in order to clarify their solute-solvent interactions, cohesive energy densities ($C_{\text{w,j}}$) for mixtures of MLPic (= j: M = Li - K; Pic⁻ = picrate ion) with water have been calculated from a modified Scatchard-Hildebrand equation.³ Based on this equation, plots of $\log K_{\text{D,MLPic}}$ versus $\log K_{\text{D,L}}$ for about ten diluents were also obtained with linear correlations,¹⁻⁴ where $K_{\text{D,j}}$ refers to a distribution constant of species j (= MLPic, L) between the two phases. From these plots satisfying the condition of $C_{\text{w,MLPic}} < C_{\text{w,L}}$, it was demonstrated that a hydrophilic L, such as 15-crown-5 (15C5) and 18-crown-6 ethers (18C6), more-strongly interacts with water molecules than do its MLPic complexes.³ Also, in the case of hydrophobic benzo-15C5 (B15C5), its ion-pair complex more-strongly interacted with w-molecules than did B15C5; that is, $C_{\text{w,B15C5}} < C_{\text{w,Li(B15C5)Pic}}$, indicating a strong hydration of Li⁺ held in B15C5.⁴ Thus, these studies for ion-pair extraction with Pic⁻ have clarified the facts that the hydrophilic properties of L control the L- and MLPic-H₂O interactions,³ while those of M^+ regulate the MLPic-H₂O ones in the case of hydrophobic L.⁴ For extraction with other A⁻, however, such studies have been scarcely done.

Also, in many cases, it is difficult to apply the same method as that of the Pic⁻ extraction systems for the other A⁻ ones, because of the low extraction ability of the latter.

In the present study, a procedure for briefly estimating the $C_{\text{w,MLA}}$ values was examined, and thereby the NaLA-H₂O interaction was discussed. So, we first determined the ion-pair formation constants (K_{MA}^0 and K_{MLA}^0) of NaO_2CCF_3 (Na^+tfa^-) and its ion-pair complexes, NaLtfa, in water at 25°C and an ionic strength (*I*) of zero by potentiometry with an ISE for Na⁺, in order to calculate the extraction constant (K_{ex}) for NaLtfa. Sodium trifluoroacetate, Natfa, in water was also extracted at 25°C by L into 1,2-dichloroethane (DCE), which was selected from satisfying the condition of $\log K_{\text{D,L}} \approx 0$ for the hydrophilic L. The three ethers described above and benzo-18C6 (B18C6) were employed as L. Secondly, the $K_{\text{D,NaLtfa}}$ values were calculated from a thermodynamic cycle¹⁻⁶ for an overall equilibrium of the ion-pair extraction. Lastly, the $C_{\text{w,NaLtfa}}$ values were estimated by using the modified equation, and then an interaction of NaLtfa with water molecules was discussed. For a comparison, the $C_{\text{w,j}}$ values for j = NaLMnO₄ and NaLReO₄ (L = 15C5, 18C6) were estimated from the extraction data^{5,6} reported previously, and accordingly the extraction experiment of NaMnO₄ by 15C5 into DCE was added.

Experimental

Chemicals

Sodium trifluoroacetate (Aldrich, 98%) was recrystallized from ethanol, filtered, and then dried *in vacuo* at 120°C for 20 h

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before use. Sodium permanganate monohydrate (Aldrich) was prepared by the common procedure.⁷ Sodium chloride (Wako, 99.98%)³ was dried at more than 140°C for 5 h. The crown ethers (15C5, 18C6, B15C5, and B18C6) were purchased from Nisso Co. Ltd., Acros, Merck, or Tokyo Chemical Industry Co. Ltd., and prepared by methods described previously.⁸ Commercially available DCE (Kanto, >99.5%) was washed three times with water,⁶ and then saturated with water before use. Other chemicals were of reagent grade and used without any purification. Water, which was passing through a Milli-Q Lab. system, was used for preparing all of the aqueous solutions in the present study.

Emf measurements

Emf measurements were performed at $25 \pm 0.3^\circ\text{C}$ in the following cell:

or

Liquid junction potentials generated at the $(\text{C}_2\text{H}_5)_4\text{NCl} | \text{test solution}$ -interface were corrected by the Henderson equation;⁹ a mobility of tfa^- in water was estimated by assuming that an ionic conductivity of tfa^- is equivalent to that¹⁰ of the trichloroacetate ion. The test solutions were an aqueous solution of NaCl for preparing a calibration curve, that of Natfa for a K_{MA} determination, and a mixture of Natfa with L at its molar ratio of unity for a K_{MLA} determination. The emf values were measured in the ranges of $[\text{Natfa}]_i = (6.8 - 81.4) \times 10^{-4} \text{ mol dm}^{-3}$ for the K_{MA}^0 determination and $[\text{Natfa}]_i = (0.3 - 11.4) \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{L}]_i = (0.3 - 11.3) \times 10^{-3}$ for the K_{MLA}^0 determination, where $[\text{L}]_i$ and $[\text{Natfa}]_i$ denote total concentrations of the corresponding species. Other procedures, ISE, the reference electrode, and apparatus employed were the same as those described previously.⁹

From potentiometrically determined $[\text{Na}^+]$, experimental K_{Natfa} and K_{NaLta} values were calculated using the equations⁹ of

$$K_{\text{MA}} = ([\text{MA}]_i - [\text{M}^+])/[\text{M}^+]^2 \text{ at } I = [\text{M}^+]$$

and

$$K_{\text{MLA}} = \frac{[\text{MA}]_i - [\text{A}^-](1 + K_{\text{MA}}[\text{M}^+])}{[\text{ML}^+][\text{A}^-]} \text{ at } I = [\text{A}^-],$$

respectively. Here, a molar concentration, $[\text{ML}^+]$, of ML^+ at equilibrium is equal to $[\text{A}^-] - [\text{M}^+]$, which is derived from a charge balance equation⁹ for the test solution. The molar concentration $[\text{A}^-]$ at equilibrium becomes the function of $[\text{M}^+]$ at $[\text{L}]/[\text{MA}]_i \approx 1$:⁹

$$[\text{A}^-] = \frac{[\text{M}^+](1 + K_{\text{ML}}[\text{M}^+])}{1 - K_{\text{ML}}K_{\text{MA}}[\text{M}^+]^2},$$

where K_{ML} denotes a complex formation constant of ML^+ in water, and is treated as a constant, as described previously.⁹

Extraction experiments

Extraction experiments were performed at $25 \pm 0.2^\circ\text{C}$ under the condition of $[\text{Natfa}]_i = 0.060 - 0.072 \text{ mol dm}^{-3}$ and $[\text{L}]_i = 0.02 - 0.15$. An experiment for the NaMnO_4 -15C5 system was also performed under the condition of $[\text{NaMnO}_4]_i = 0.011 \text{ mol}$

Fig. 1 Plots of $\log(K_{\text{Natfa}}/y^2)$ vs. $(y[\text{Na}^+])^2$.

dm^{-3} and $[\text{15C5}]_i = 0.010 - 0.046$. The apparatuses used were the same as those⁶ described previously.

The operations were as follows. An aqueous solution (12 cm^3) of Natfa or NaMnO_4 with L was mixed with a DCE (12 cm^3) saturated with water in a stoppered glass tube, and then shaken at 25°C for 2 h or 10 min, respectively.⁶ After the extraction of NaLA into DCE, the mixture was centrifuged, a $4 - 10 \text{ cm}^3$ portion of the DCE-phase was separated, and all NaLA in this portion was back-extracted into $8 - 20 \text{ cm}^3$ of water. The NaLA complex was extracted thoroughly by two-time back-extraction. Its Na concentrations ($\approx [\text{NaLA}]_o$) were determined at 589.0 nm by AAS, and then corrected by blank experiments. Here, the symbol $[j]_o$ denotes a concentration of j ($= \text{NaLA}, \text{L}$) at equilibrium in the o-phase. Based on the above experiments, an experimental distribution ratio (D^{expl}) of Na was calculated from the equation

$$D^{\text{expl}} = [\text{NaLA}]_o / ([\text{NaA}]_i - [\text{NaLA}]_o) \\ = \{[\text{NaLA}]_o / ([\text{Na}^+] + [\text{NaA}] + [\text{NaL}^+] + [\text{NaLA}])\}^5.$$

The extraction constant K_{ex} has been defined as $[\text{MLA}]_o / ([\text{M}^+][\text{L}]_o[\text{A}^-])$,^{1,2} which is based on the following component equilibrium ones: namely,

$$K_{\text{D,L}} = [\text{L}]_o / [\text{L}]; \\ K_{\text{ML}} = [\text{ML}^+] / [\text{M}^+][\text{L}]; \\ K_{\text{MLA}} = [\text{MLA}] / [\text{ML}^+][\text{A}^-]; \\ K_{\text{D,MLA}} = [\text{MLA}]_o / [\text{MLA}]; \text{ then} \\ K_{\text{ex}} = K_{\text{ML}}K_{\text{MLA}}K_{\text{D,MLA}}/K_{\text{D,L}}.$$

Taking logarithms of both sides of the thus-defined K_{ex} equation and rearranging it, we can obtain an equation of $\log(D_{\text{M}}/[\text{A}^-]) = \log K_{\text{ex}} + \log[\text{L}]_o$ with $D_{\text{M}} = [\text{MLA}]_o/[\text{M}^+]$. Thereby, a composition of the extracted species has been determined^{1,2,4} (see Fig. 3). As a relation between D_{M} and D^{expl} , the following one⁵ was employed:

$$D^{\text{expl}} = D_{\text{M}} / \{1 + K_{\text{MA}}[\text{A}^-] + (K_{\text{ML}}[\text{L}]_o/K_{\text{D,L}})(1 + K_{\text{MLA}}[\text{A}^-])\}.$$

The I values of the w-phase was expressed at $[\text{A}^-] \{= (1/2)([\text{M}^+] + [\text{ML}^+] + [\text{A}^-])\}$.⁵ Other procedures and a method for calculating K_{ex} from $[\text{Natfa}]_i$, $[\text{L}]_i$, and D^{expl} were the same as those⁴ described previously.

Fig. 2 Plots of $\log(K_{\text{NaLtfa}}/y^2)$ vs. $y^2[\text{NaL}^+][\text{tfa}^-]$ for $L = \text{B15C5}$.

Results and Discussion

Ion-pair formation of Natfa and NaLtfa complexes in water

The $\log(K_{\text{NaLtfa}}/y^2)$ values were plotted against the $(y[\text{Na}^+])^2$ values (Fig. 1). Here, y denotes a mean ionic activity coefficient, which was estimated from the Debye-Hückel limiting law or the Davies equation. The plot in Fig. 1 was analyzed by a non-linear regression using the equation

$$\log \frac{K_{\text{NaLtfa}}}{y^2} = \log \left\{ K_{\text{NaLtfa}}^0 + \frac{b}{(y[\text{Na}^+])^2} \right\},$$

where b refers to an empirical parameter¹¹ for a curve-fitting and corresponds an apparent concentration of MA lost from the bulk of the aqueous solution in the potentiometric measurements, as described previously.^{3,9} A regression analysis of the plots gives

$$\begin{aligned} K_{\text{NaLtfa}}^0 (\equiv y_0[\text{Natfa}]/y^2[\text{Na}^+][\text{tfa}^-] = K_{\text{NaLtfa}}/y^2 \text{ at } y_0 \approx 1) \\ = 4.0 \pm 0.8 \text{ mol}^{-1} \text{ dm}^3 \end{aligned}$$

and

$$b = (1.4 \pm 0.07) \times 10^{-4} \text{ mol dm}^{-3}$$

with a hyperbola-like curve (solid line in Fig. 1) of a correlation coefficient (R) = 0.963 at a number of data (n) of 76. Similarly, hyperbola-like curves were obtained from plots of $\log(K_{\text{NaLtfa}}/y^2)$ versus $y^2[\text{NaL}^+][\text{tfa}^-]$ with $L = 15\text{C5}$, B15C5 (Fig. 2), 18C6 , and B18C6 . These plots were analyzed by curve-fitting to the equation of

$$\log \frac{K_{\text{NaLtfa}}}{y^2} = \log \left\{ K_{\text{NaLtfa}}^0 + \frac{b_m}{y^2[\text{NaL}^+][\text{tfa}^-]} \right\},^9$$

where K_{NaLtfa}^0 is defined as $y_0[\text{NaLtfa}]/y^2[\text{NaL}^+][\text{tfa}^-]$ ($= K_{\text{NaLtfa}}/y^2$ at $y_0 \approx 1$). The solid line in Fig. 2 represents the result based on such analysis. The analysis yielded $K_{\text{Na(15C5)tfa}}^0 = 511 \pm 88 \text{ mol}^{-1} \text{ dm}^3$ and an empirical curve-fitting parameter (b_m),¹¹ similar to b , $= (9.6 \pm 0.8) \times 10^{-5} \text{ mol dm}^{-3}$ with $R = 0.968$ at $n = 55$; $K_{\text{Na(B15C5)tfa}}^0 = 119 \pm 88$ and $b_m = (2.9 \pm 0.2) \times 10^{-4}$ with 0.989 at 27; $K_{\text{Na(18C6)tfa}}^0 = 384 \pm 67$ and $b_m = (1.4 \pm 0.1) \times 10^{-4}$ with 0.986 at 73; $K_{\text{Na(B18C6)tfa}}^0 = 201 \pm 25$ and $b_m = (2.1 \pm 0.2) \times 10^{-4}$ with 0.983 at 45.

The K_{NaLtfa}^0 values were much larger than the K_{Natfa}^0 one. This is similar to those for other systems reported before.^{6,9} Its finding

Fig. 3 Plots of $\log(D_{\text{Na}}/[\text{tfa}^-])$ vs. $\log[L]_o$ for $L = 15\text{C5}$ (○), B15C5 (□), 18C6 (●), and B18C6 (■). The broken lines correspond to the plots for the 18C6 derivatives.

shows at least that the complex formation of Na^+ with L in water weakens hydration around Na^+ . Also, we can see from the K_{NaLtfa}^0 values that the ion-pair complexes with the more-bulky L have the smaller K_{NaLtfa}^0 values, except for a relationship between the mono-benzo ethers: $15\text{C5} > \text{B15C5}$, $18\text{C6} > \text{B18C6}$, and $15\text{C5} > 18\text{C6}$. These results seemingly indicate that the substitution by a benzo group and the increasing ring size are effective for reducing the ion-pair formation-ability of NaL^+ in water. This is predictable from the Coulombic interaction between NaL^+ and tfa^- .¹² On the other hand, the relationship between the mono-benzo ethers was $\text{B15C5} < \text{B18C6}$. This fact suggests that a shielding effect of a charge on Na^+ by B15C5 is larger than that by B18C6 , because hydrophobic effects predicted from the $\log K_{\text{D,L}}$ values are nearly equal between their L (see Table 1). This is supported by the fact that the number (0.8) of water molecules co-extracted with Na(B15C5)^+ into nitrobenzene is somewhat smaller than that (1.1) with Na(B18C6)^+ .¹³

Extraction of Natfa by L into DCE

Figure 3 shows plots of $\log(D_{\text{Na}}/[\text{tfa}^-])$ versus $\log[L]_o$ for the four L systems (see the experimental section). Under the experimental conditions of $[\text{Natfa}]_t$ and $[L]_o$, the slopes of the plots were about unity (0.981 – 1.08) for all of the systems, indicating an extraction of 1:1:1 ion-pair complexes into the DCE-phase, and their straight lines gave R of 0.959 – 0.982. Also, a straight line with a slope = 0.999, at $R = 0.987$ and $n = 16$ was obtained for the NaMnO_4 - 15C5 system. The $\log K_{\text{ex}}$ values calculated from each point of these plots are listed in Table 1, together with the component equilibrium constants,^{1,2,14,15} which correspond to each system. It is clear that a difference in $\log K_{\text{ex}}$ between the MnO_4^- and tfa^- extraction systems is mainly due to that in $\log K_{\text{D,Na(15C5)A}}$ between them.

The $\log K_{\text{ex}}$ values at $A^- = \text{tfa}^-$ were on the order of $\text{B15C5} \approx \text{B18C6} < 18\text{C6} < 15\text{C5}$ (Table 1). This order is consistent with that of the $\log K_{\text{NaLtfa}}$ values, and close to the order of the $-\log K_{\text{D,L}}$ ones. These results indicate that the extraction-abilities of these L are controlled largely by both the ion-pair formation of NaLtfa in the w-phase and the distribution of L between the two phases. This case is similar to that for the NaReO_4 - L extraction system. Also, the extraction-ability of the

Table 1 Equilibrium constants for the extraction of NaA by L into DCE and their component equilibrium ones at 25°C

NaA-L (<i>I</i> ^a)	log <i>K</i> _{ex} ^b	log <i>K</i> _{ML} ^c	log <i>K</i> _{MLA} ^d	log <i>K</i> _{D,MLA} ^e	−log <i>K</i> _{D,L} ^f
Natfa-15C5 (0.040)	0.36 ± 0.06	0.70	2.55	−2.87	−0.02
−B15C5 (0.061)	−0.88 ± 0.04	0.45	1.89	−1.31	−1.910
−18C6 (0.038)	−0.07 ± 0.07	0.73	2.43	−3.20	−0.03
−B18C6 (0.054)	−0.86 ± 0.06	0.81	2.13	−1.79	−2.009
NaMnO ₄ -15C5 (0.010)	2.02 ± 0.03	0.70	1.49	−0.15	−0.02

a. Average values of the w-phase which were calculated in mol dm^{−3} unit. b. Average ± standard deviation. c. See Ref. 14 for the values. d. Estimated from the *K*_{MLA} values at *I* using *K*_{MLA} = *y*²*K*_{MLA}⁰. See Ref. 5. The log *K*_{NaLtf} values deviated by ±0.03 at their maxima in the range of *I* = 0.04 to 0.06 and also the log *K*_{Na(15C5)MnO₄} value at *I* = 0.040 was estimated to be 1.42. e. Calculated from the thermodynamic cycle, log *K*_{D,MLA} = log *K*_{ex} + log *K*_{D,L} − log *K*_{ML} − log *K*_{MLA}. See Refs. 1 and 2. f. Refs. 1, 2, and 15.

present Natfa-L system is characterized by the much lower log *K*_{D,NaLA} values than the values² of the NaPic-L system. Taking account of the donor abilities of DCE and H₂O, this should reflect an interaction of NaLtf with water molecules in the w-phase (see below).

The log *K*_{ex}-relationship of 18C6 < 15C5 is mainly due to the difference (= −2.87 + 3.20 = 0.33) in log *K*_{D,NaLtf} between these NaLtf (Table 1). Similarly, the relationship of B18C6 < 18C6 is due to the difference (1.98) in log *K*_{D,L} between their L. These trends are similar to those for both the NaPic- and NaReO₄-L systems.^{3,5} On the other hand, there is no difference (| 0.02 |) in log *K*_{ex} between the mono-benzo ethers; a difference (= 0.60) in the sum of log *K*_{NaL} and log *K*_{NaLtf} almost cancels out that (= −0.58) in the sum of log *K*_{D,NaLtf} and log *K*_{D,L} (Table 1). This fact is different from those for the above two systems. Namely, a difference (= 0.26) in log *K*_{ex} for the Pic[−] systems³ is mostly due to that in log *K*_{D,NaLPic} [log{*K*_{D,Na(B15C5)Pic}/*K*_{D,Na(B18C6)Pic}} = 0.54], while it (= 0.64) for the ReO₄[−] systems is due to a difference in log *K*_{NaLReO₄} [log{*K*_{Na(B18C6)ReO₄}/*K*_{Na(B15C5)ReO₄}} = 0.79].¹⁶

Estimation of cohesive energy densities

Experimental plots based on the modified Scatchard-Hildebrand equation,³ which is described with the following equations, have shown that the *V*_{MLA}/*V*_L values are in the range of 1.1 to 1.9^{3,4} for the MPic-15C5 and −18C6 extraction systems with M = Li to Rb (lack of the LiPic-15C5 one) being about ten diluents.

$$\log K_{D,MLA} = (V_{MLA}/V_L)(\log K_{D,L} + \beta) \quad (1)$$

with

$$\beta = \frac{2V_L}{2.303RT} \{ (C_{w,L} - C_{w,MLA}) - (C_{o,L} - C_{o,MLA}) \}. \quad (1a)$$

Here, *V*_j and *C*_{ij} denote the molar volume (cm³ mol^{−1}) of j (= MLA, L) and the cohesive energy density (J cm^{−3}) for the mixture of i (= w, o) with j, respectively. From the results of *V*_{MLPic}/*V*_L, we can easily suppose that the plots for the NaA-15C5 and −18C6 systems with A[−] = MnO₄[−], ReO₄[−], and tfa[−] yield slopes being close to those of the plots for the systems with Pic[−]. Also, both the log *K*_{D,15C5} and log *K*_{D,18C6} values nearly equal zero for the w/DCE extraction systems (see Table 1). Accordingly, the log *K*_{D,NaLA} values calculated for the w/DCE systems should be very close to the intercepts of straight lines composed of the log *K*_{D,NaLA} versus log *K*_{D,L} plots. This means that the log *K*_{D,MLA} values at the present systems with the hydrophilic L are related to the β ones by the equation of log *K*_{D,MLA} ≈ *V*_{MLA}β/*V*_L, which is derived from Eq. (1). Including the log *K*_{D,NaLA} values^{3,5} reported before, an order of their values around log *K*_{D,L} = 0 was A[−] = tfa[−] < ReO₄[−] < MnO₄[−] (≈ 0) < Pic[−]. The same order was observed

Table 2 Cohesive energy densities for the mixtures of L or NaLA with water molecules at 25°C

j	<i>C</i> _{wj} /kJ cm ^{−3}	
	L = 15C5	18C6
NaLPic ^a	0.944	0.936
L ^a	0.967	0.953
NaLMnO ₄	0.96 ₉	0.95 ₈
NaLReO ₄	0.98 ₀	0.96 ₃
NaLtf	0.99 ₆	0.99 ₂

a. Ref. 3.

around log *K*_{D,L} = 2 for the mono-benzo derivatives employed, except for the MnO₄[−] systems, which lack extraction data. When | *C*_{w,L} − *C*_{w,NaLtf} | ≫ | *C*_{DCE,L} − *C*_{DCE,NaLtf} | in β, as described before,³ the order indicates that the tfa[−] systems satisfy the condition *C*_{w,L} < *C*_{w,NaLtf}, while the Pic[−] ones satisfy *C*_{w,L} > *C*_{w,NaLPic}. Namely, the NaLtf ion-pair complexes most-strongly interact with water molecules in the NaLA complexes, while the NaLPic complexes most-weakly interact with the w-ones.

We have estimated so far the *C*_{w,MLA} values using the modified form^{3,4} of Eq. (1a):

$$C_{w,MLA} \approx C_{w,L} - 2.303RT\beta/2V_L. \quad (2)$$

The estimates of β can be obtained from the equation log *K*_{D,NaLA} ≈ *V*_{NaLA}β/*V*_L by assuming that the *V*_{NaLA}/*V*_L values are close to 1.5 to 1.6 of the MPic-15C5 system (M = Na, K) and 1.1 to 1.2 of the MPic-18C6 one (M = Li - K).³ Here, the larger *V*_{NaLA}/*V*_L values must be valid for this estimation, because the log *K*_{D,NaLA} values calculated at log *K*_{D,L} = 0.02 or 0.03 (Table 1) are over-estimates as the *V*_{NaLA}β/*V*_L values (intercepts). Introducing *C*_{w,15C5} = 0.967 kJ cm^{−3} (Ref. 3) or *C*_{w,18C6} = 0.953,³ *V*_{15C5} = 189 cm³ mol^{−1} (Ref. 2) or *V*_{18C6} = 214,¹ and the β estimates into Eq. (2), the *C*_{w,NaLA} values were 0.96₉ kJ cm^{−3} for NaLA = Na(15C5)MnO₄, 0.98₀ for Na(15C5)ReO₄, 0.99₆ for Na(15C5)tfa and 0.95₈ for Na(18C6)MnO₄, 0.96₃ for Na(18C6)ReO₄, 0.99₂ for Na(18C6)tfa. These values are listed in Table 2. The values increased in going from NaLPic to NaLtf. Also, the values for 15C5 and their NaLA complexes were slightly larger than those for 18C6 and its complexes, respectively. A dependence of *C*_{w,NaLA} on *I* was not observed in the range of 0.005₈ to 0.044 mol dm^{−3}.

Interaction between NaLA and water molecules

The *C*_{w,NaLtf} values were larger than the *C*_{w,L} ones for a given L (Table 2). This suggests that there is some interaction, such as hydrogen bonding and a dipole-dipole interaction, between H₂O

and NaLtfa in the w-phases; for example, such as $\text{NaL}^+\cdot\text{O}_2\text{CCF}_3\cdots\text{H}_2\text{O}$ and/or $\text{NaL}^+\cdot\text{F}_3\text{CCO}_2\cdots\text{H}_2\text{O}$. Such an interaction may come from a less-symmetrical structure (point group: C_s^{17}) of tfa^- than that (T_d) of MO_4^- with $M = \text{Mn}$ and Re and a polarity of tfa^- . The former property suggests a difference in the geometrical structure between NaLtfa and NaLMO_4 to us. For the latter, the electronegativities of the CF_3 and COO^- groups were estimated to be 10.90 ($= 3.46^{18}$ in Pauling unit) and 4.19, respectively, when a calculation method¹⁸ developed by Huheey was used. Similarly, there seems to be a slight difference between $C_{w,\text{NaLA}}$ for the other A^- systems and $C_{w,L}$ (Table 2).

As can be seen from Table 2, the $C_{w,j}$ values estimated above are in the trend of $j = \text{NaLPic} < L \leq \text{NaLMnO}_4 \leq \text{NaLReO}_4 < \text{NaLtfa}$ at the hydrophilic L. This finding means that the interaction of NaLA with water molecules increases in going from NaLPic to NaLtfa. Also, the trend is in good agreement with the reverse order of the $\log K_{D,L}$ and $\log K_{D,\text{NaLA}}$ values: Na(15C5)Pic ($\log K_{D,j} = 2.46$ (Ref. 3)) $> 15\text{C5}$ (0.02 (Ref. 2)) $> \text{Na(15C5)MnO}_4$ (-0.15) $> \text{Na(15C5)ReO}_4$ (-1.29 (Ref. 19)) $> \text{Na(15C5)tfa}$ (-2.87) and Na(18C6)Pic (1.49 (Ref. 3)) $> 18\text{C6}$ (0.03) $> \text{Na(18C6)MnO}_4$ (-0.42 (Ref. 5)) $> \text{Na(18C6)ReO}_4$ (-0.79 (Ref. 19)) $> \text{Na(18C6)tfa}$ (-3.20). Thus, the $\log K_{D,\text{NaLA}}$ values of the present ion-pair extraction system can reflect the interaction between MLA and H_2O in the w-phases. These facts also indicate that a hydrophilic property of A^- increases in the order of $A^- = \text{Pic}^- < \text{MnO}_4^- < \text{ReO}_4^- < \text{tfa}^-$, since NaL^+ is being fixed at $L = 15\text{C5}$ or 18C6 . The same can be true of NaLA with $L = \text{B15C5}$ or B18C6 , because this order corresponds with the reverse order, $\text{Pic}^- < \text{ReO}_4^- < \text{tfa}^-$, of $\log K_{D,\text{NaLA}}$ around $\log K_{D,L} = 2$.

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