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Thermodynamic Study on Solvent Extraction of 18-Crown-6-Alkali Metal Ion Complexes and Tetraalkylammonium Ions with Picrate Anions into Benzene

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Enthalpy and entropy changes for ion-pair extractions of tetraalkylammonium ions (Me_4N^+, Et_4N^+, n-Pr_4N^+, n-Bu_4N^+) with picrate anions, overall extractions of alkali metal (Na, K, Rb, Cs) picrates with 18-crown-6 (18C6), and distribution of 18C6 itself were determined between benzene and water, Me, Et, *n*-Pr, and *n*-Bu denoting methyl, ethyl, propyl, and butyl groups, respectively. All the extracted 18C6 complexes were 1:1:1 complexes (alkali metal ion:18C6:picrate anion). The values of enthalpy and entropy changes are negative for overall extractions of all the alkali metal picrates with 18C6. Plots of thermodynamic quantities for ion-pair extractions of R_4NA vs. the number of carbon atoms of R_4N^+ show a linear relationship, R_4N^+ and A^- being tetraalkylammonium ion and picrate anion, respectively. Enthalpy and entropy changes were calculated for ion-pair extractions of 18C6–alkali metal ion complexes with picrate anions. The thermodynamic parameters for ion-pair extractions of 18C6–alkali metal picrate complexes were compared with those of R_4NA, and were discussed in detail from the standpoint of molecular grounds. It was found from these data that the 18C6–K^+ complex acts as a structure breaker in water.

Numerous data have been presented on complexing power of crown compounds for metal ions. However, a few reports have been published on solvation properties of the crown compound complexes. Ion-pair extraction study of crown compound complexes provides very valuable information on solute-solvent interaction of the crown compound complexes in water.[1)]

One of the principal objects of this paper is to investigate solvation behavior of the crown compound complexes in water. In the present work, enthalpy and entropy changes for ion-pair extraction of 18-crown-6 (18C6)–alkali metal ion complexes and tetraalkylammonium ions (R_4N^+) with picrate anions (A^-) have been determined between benzene and water. Thermodynamic quantities for ion-pair extraction of 18C6- and 15-crown-5 (15C5)–alkali metal picrate complexes were compared with those of R_4NA, and were discussed in detail from the standpoint of molecular grounds.

Experimental

Materials. Tetramethyl-, tetraethyl-, tetrapropyl-, and tetrabutylammonium hydroxides (Wako-Pure Chemicals Ltd.) were used as received. 18-Crown-6 (Nisso Co., Ltd.) was recrystallized from acetonitrile and, prior to use, dried at 80 °C in vacuo. Benzene, picric acid, $LiOH \cdot H_2O$, NaOH, and KOH were analytical grade reagents. Rubidium and caesium hydroxides were of reagent grade. Benzene was washed three times with distilled water.

Extraction Procedure. (1) Ion-pair extraction of tetraalkylammonium picrate. A benzene phase and an aqueous phase of R_4NOH (1.7×10^{-4}—3.2×10^{-2} M[†]), LiOH (0.1 M), and picric acid (4.2×10^{-5}—5.1×10^{-3} M) in stoppered glass tubes (30 ml) or Erlenmeyer flasks with stoppers (300 ml) were shaken for 2 h in a water bath thermostated at 20, 25, 30, 35, and 40±0.2 °C, and centrifuged. For Et_4NA, n-Pr_4NA, and n-Bu_4NA systems, the initial volume of each phase was 12 ml, whereas, for the Me_4NA system, those of benzene and aqueous phases were 200 and 20 ml, respectively. Extractions were conducted at pH 12.5—13.1. A portion of the benzene phase (10 ml for the former systems and 100 ml for the latter system) was transferred to a beaker and allowed to evaporate over several days. The residue was dissolved in 0.01 M NaOH aqueous solution (4 ml) and the picrate concentration was determined spectrophotometrically at 356 nm ($\varepsilon = 1.45 \times 10^4$ cm^{-1} M^{-1}). (2) Extraction of alkali metal picrates with 18C6. Experimental procedures and concentrations of 18C6, alkali metal hydroxides, and picric acid were almost the same as those described in a previous paper.[2)] Extractions were performed at pH 11.1—12.3 at 20, 30, 35, and 40±0.2 °C.

The Distribution Coefficient of 18C6. A 12 ml benzene solution of 18C6 (2.0×10^{-5}—9.3×10^{-4} M) and an equal volume of distilled water in a stoppered glass tube were shaken in a thermostated water bath for 1 h and centrifuged. A portion (11 ml) of the benzene phase and an equal volume of aqueous solution (pH 11.7—12.3) of KOH (3×10^{-2} M) and picric acid (8×10^{-3} M) were placed in a stoppered glass tube and agitated. After centrifuging, the picrate in the benzene phase was back-extracted into 8 ml of 0.01 M NaOH aqueous solution, and the picrate concentration was determined spectrophotometrically ($\lambda_{max} = 356$ nm, $\varepsilon = 1.45 \times 10^4$ cm^{-1} M^{-1}). Experiments were carried out at 20, 30, 35, and 40±0.2 °C. Each distribution coefficient value of 18C6 is the average of about seven measurements.

Results

Ion-Pair Extraction of R_4NA. In an equilibrium between benzene and an aqueous solution of R_4NA, the equilibrium constants are defined as

$$K_A(R_4NA) = [R_4NA]/[R_4N^+][A^-], \qquad (1)$$

$$K_D(R_4NA) = [R_4NA]_o/[R_4NA], \qquad (2)$$

[†] 1 M=1 mol dm^{-3}.

$$K_{\mathrm{ex,ip}}(\mathrm{R_4NA}) = [\mathrm{R_4NA}]_\mathrm{o}/[\mathrm{R_4N^+}][\mathrm{A^-}] = K_\mathrm{A}(\mathrm{R_4NA})K_\mathrm{D}(\mathrm{R_4NA}), \quad (3)$$

where the subscript "o" and the lack of subscript denote the organic and aqueous phases, respectively. The distribution ratio of $\mathrm{R_4N^+}$ is represented by

$$D = [\mathrm{R_4NA}]_\mathrm{o}/([\mathrm{R_4N^+}] + [\mathrm{R_4NA}]). \quad (4)$$

Combination of Eqs. 1—4 leads to

$$D^{-1} = K_\mathrm{D}(\mathrm{R_4NA})^{-1} + (K_{\mathrm{ex,ip}}(\mathrm{R_4NA})[\mathrm{A^-}])^{-1}. \quad (5)$$

A plot of D^{-1} against $[\mathrm{A^-}]^{-1}$ shows a straight line in every case. Values of $K_{\mathrm{ex,ip}}(\mathrm{R_4NA})$ were calculated from the slopes of these straight lines. $K_\mathrm{D}(\mathrm{R_4NA})$ and $K_\mathrm{A}(\mathrm{R_4NA})$ values could be obtained only for the n-$\mathrm{Bu_4NA}$ system at 25 °C ($K_\mathrm{D}=4$, $K_\mathrm{A}=1.4\times10^3$). K_D values of n-$\mathrm{Bu_4NA}$ and K(18C6)A (3.7[3]) are almost the same, but, K_A value of n-$\mathrm{Bu_4NA}$ is one order of magnitude over that of K(18C6)A (140[3]).

$R\ln K_{\mathrm{ex,ip}}(\mathrm{R_4NA})$ vs. T^{-1} plots are found to be linear in every system. Enthalpy change ($\Delta H_{\mathrm{ex,ip}}(\mathrm{R_4NA})$) and entropy change ($\Delta S_{\mathrm{ex,ip}}(\mathrm{R_4NA})$) for Eq. 3 were calculated from these data. The thermodynamic quantities are listed in Table 1.

Extraction of Alkali Metal Picrates with 18C6. When an equilibrium is established between an aqueous phase of alkali metal ion ($\mathrm{M^+}$) and picrate ion, and a benzene phase of crown ether (L), the equilibrium constants are defined as

$$K_\mathrm{ex} = [\mathrm{MLA}]_\mathrm{o}/[\mathrm{M^+}][\mathrm{L}]_\mathrm{o}[\mathrm{A^-}], \quad (6)$$

$$K_\mathrm{D}(\mathrm{L}) = [\mathrm{L}]_\mathrm{o}/[\mathrm{L}], \quad (7)$$

$$K_\mathrm{ML} = [\mathrm{ML^+}]/[\mathrm{M^+}][\mathrm{L}], \quad (8)$$

$$K_{\mathrm{ex,ip}}(\mathrm{MLA}) = [\mathrm{MLA}]_\mathrm{o}/[\mathrm{ML^+}][\mathrm{A^-}]. \quad (9)$$

Thus, K_ex can be written as

$$K_\mathrm{ex} = K_\mathrm{ML}\cdot K_{\mathrm{ex,ip}}(\mathrm{MLA})\cdot K_\mathrm{D}(\mathrm{L})^{-1}. \quad (10)$$

The distribution ratio of the alkali metal is represented by

$$D = [\mathrm{MLA}]_\mathrm{o}/[\mathrm{M^+}]. \quad (11)$$

Combination of Eqs. 6 and 11 leads to

$$D = K_\mathrm{ex}[\mathrm{L}]_\mathrm{o}[\mathrm{A^-}]. \quad (12)$$

Log ($D/[\mathrm{A^-}]$) vs. log $[\mathrm{L}]_\mathrm{o}$ plots give a straight line with a slope of 1 in every case. This indicates that the K_ex can be described by Eq. 6. The values of $[\mathrm{L}]_\mathrm{o}$ and $[\mathrm{A^-}]$ in Eq. 12 were calculated by

$$[\mathrm{L}]_\mathrm{o} = ([\mathrm{L}]_\mathrm{t} - [\mathrm{MLA}]_\mathrm{o})/(1 + K_\mathrm{D}(\mathrm{L})^{-1}), \quad (13)$$

$$[\mathrm{A^-}] = [\mathrm{HA}]_\mathrm{t} - [\mathrm{MLA}]_\mathrm{o}, \quad (14)$$

where the subscript "t" refers to the total concentration.

$R\ln K_\mathrm{D}(\mathrm{L})$ vs. T^{-1} and $R\ln K_\mathrm{ex}$ vs. T^{-1} plots show a linear relationship in every system. Enthalpy and entropy change for Eqs. 6 and 7 were calculated from these data in the same manner as that mentioned above. The thermodynamic parameters are summarized in Table 2.

Discussion

Ion-Pair Extraction of $\mathrm{R_4NA}$. It can be seen from log $K_{\mathrm{ex,ip}}$ values in Table 1 that the larger the size of $\mathrm{R_4N^+}$ is, the more extractable into benzene it is. Plots of log $K_{\mathrm{ex,ip}}(\mathrm{R_4NA})$ against the number of carbon atoms of $\mathrm{R_4N^+}$ give a straight line with a slope of

Table 1. Thermodynamic Quantities for Ion-Pair Extraction of Tetraalkylammonium Picrates between Benzene and Water

	$\log(K_{\mathrm{ex,ip}}$/ $\mathrm{mol^{-1}\,dm^3}$) (at 25°C)	$\Delta H^\circ_{\mathrm{ex,ip}}$/ $\mathrm{kJ\,mol^{-1}}$	$T\Delta S^\circ_{\mathrm{ex,ip}}$/ $\mathrm{kJ\,mol^{-1}}$ (at 25°C)
$\mathrm{Me_4NA}$	−2.06	0	$-12._1$
$\mathrm{Et_4NA}$	−0.60	5.3	1.8
n-$\mathrm{Pr_4NA}$	1.61	$10._3$	$19._5$
n-$\mathrm{Bu_4NA}$	3.67	$15._1$	$35._8$

Table 2. Thermodynamic Quantities for Extraction of Alkali Metal Picrates with 18C6 between Benzene and Water

log $K_\mathrm{D}(\mathrm{L})$[a,2] $= -1.19_8$			
	log K_ex[a,2]	log K_ML[a]	log $K_{\mathrm{ex,ip}}$[a,2]
Na	3.39	0.80[4]	1.39
K	5.97	2.03[4,5]	2.74
Rb	5.43	1.56[4]	2.67
Cs	4.38	0.99[4]	2.19
$\Delta H^\circ_\mathrm{D}(\mathrm{L})/\mathrm{kJ\,mol^{-1}} = 37._6$		$T\Delta S^\circ_\mathrm{D}(\mathrm{L})/\mathrm{kJ\,mol^{-1}}$[a] $= 30._4$	
$\Delta H^\circ/\mathrm{kJ\,mol^{-1}}$[b]			
	$\Delta H^\circ_\mathrm{ex}$	$\Delta H^\circ_\mathrm{ML}$	$\Delta H^\circ_{\mathrm{ex,ip}}$
Na	$-34._4$	−9.41[4]	$12._6$
K	$-77._3$	−25.01[5]	$-14._6$
Rb	$-77._6$	−16.0[4]	$-24._0$
Cs	$-66._3$	−15.9[4]	$-12._8$
$T\Delta S^\circ/\mathrm{kJ\,mol^{-1}}$[a,c]			
	$T\Delta S^\circ_\mathrm{ex}$	$T\Delta S^\circ_\mathrm{ML}$	$T\Delta S^\circ_{\mathrm{ex,ip}}$
Na	$-14._7$	−4.6[4]	$20._3$
K	$-42._8$	−13.22[5]	0.8
Rb	$-46._1$	−7.1[4]	$-8._6$
Cs	$-40._9$	−10[4]	−0.5

a) at 25°C.

b) $\Delta H^\circ_\mathrm{ex} = -\Delta H^\circ_\mathrm{D}(\mathrm{L}) + \Delta H^\circ_\mathrm{ML} + \Delta H^\circ_{\mathrm{ex,ip}}$.

c) $\Delta S^\circ_\mathrm{ex} = -\Delta S^\circ_\mathrm{D}(\mathrm{L}) + \Delta S^\circ_\mathrm{ML} + \Delta S^\circ_{\mathrm{ex,ip}}$, where subscripts "ex, D, ML, and ex,ip" refer to reactions represented by Eqs. 6—9, respectively.

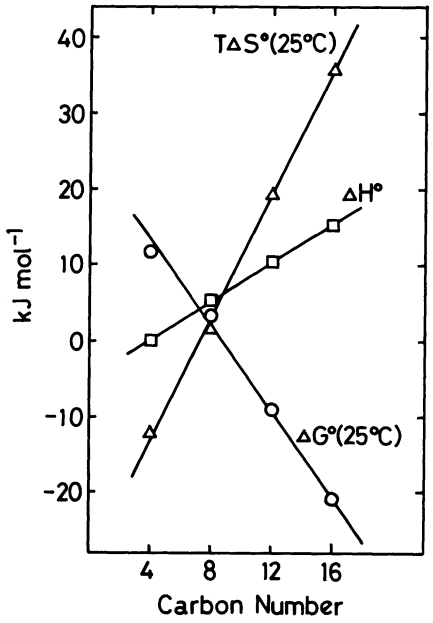

Fig. 1. Plots of thermodynamic parameters for ion-pair extraction of R_4NA vs. the number of carbon atoms of R_4N^+.

0.48_5. This indicates that the contribution of a methylene group to extraction constants of ion-pairs (Π_{CH_2}) at 25 °C between benzene and water is 0.48_5. The Π_{CH_2} value determined from the extraction of ion-pairs of alkanesulfonate ions with cationic dyes between benzene and water at 25 °C has been reported to be 0.64,[6] and is larger than that of this study. This may be due largely to the difference in the shape of tetraalkylammonium and alkanesulfonate ions.

Plots of thermodynamic parameters for ion-pair extraction of R_4NA vs. the number of carbon atoms of R_4N^+ in Fig. 1 show a linear relationship. Contributions of a methylene group to ΔH and ΔS of ion-pair extraction ($\Delta H_{ex,ip}(CH_2)$ and $\Delta S_{ex,ip}(CH_2)$) between benzene and water were found from the slopes to be 1.2_5 kJ mol^{-1} and $13._5$ J K^{-1} mol^{-1}, respectively. Positive $\Delta H_{ex,ip}(CH_2)$ and $\Delta S_{ex,ip}(CH_2)$ values suggest that a methylene group may undergo hydrophobic hydration in the aqueous phase. From values of enthalpy and entropy changes of hydration of hydrocarbons (methane–butane),[7] enthalpy and entropy increments per methylene group were calculated to be -3.63 kJ mol^{-1} and -12.5 J K^{-1} mol^{-1}, respectively. Values of $\Delta H_{ex,ip}(CH_2)$ and $\Delta S_{ex,ip}(CH_2)$ determined in this work are comparable to the reported values. It follows from this finding that dehydration of CH_2 plays a very important role in the transfer equilibrium of CH_2 from water to benzene. The value of $T\Delta S_{ex,ip}(CH_2)$ at 25 °C is 3.2 times larger than that of $\Delta H_{ex,ip}(CH_2)$. This indicates that when the alkyl chain in R_4N^+ lengthens, an increase in extractability of R_4NA is largely entropy controlled.

Table 1 shows that the ion-pair extraction process of n-Pr_4NA and n-Bu_4NA is mostly entropy controlled, resulting in the positive $\log K_{ex,ip}$ values, whereas, for Me_4NA and Et_4NA, unfavorable entropy and enthalpy change cause the negative $\log K_{ex,ip}$ values, respectively.

The larger the size of R_4N^+, the greater the $\Delta S_{ex,ip}$ value and the more endothermic is the ion-pair extraction process of R_4NA ($\Delta H_{ex,ip}=0$ for Me_4NA). The negative $\Delta S_{ex,ip}$ value is observed only for Me_4NA. This tendency seems to reflect the change from structure-breaking effect of Me_4N^+ to structure-making effect of n-Bu_4N^+ in an aqueous solution.[8]

A plot of $\Delta H_{ex,ip}$ against reciprocal of the radius of R_4N^+ shows a better linear relationship compared to the case of $\Delta S_{ex,ip}$ (correlation coefficient $r=-0.992$ and -0.983 for $\Delta H_{ex,ip}$ and $\Delta S_{ex,ip}$, respectively). This indicates that $\Delta H_{ex,ip}$ is composed more largely of electrostatic interaction compared to $\Delta S_{ex,ip}$.

Distribution of Crown Ethers. Values of $\log K_D(L)$ at 25 °C of 12-crown-4 (12C4) and 15C5 between benzene and water are -0.82[9] and -0.80_6,[2] respectively. From $\log K_D(L)$ values of 12C4, 15C5, and 18C6, the contribution of an ether oxygen atom to $\log K_D(L)$ (Π_o) at 25 °C between benzene and water can be evaluated by means of Π_{CH_2} value determined in this work ($\Pi_o=(\log K_D(L)-\Pi_{CH_2}\times a)\div b$, a and b being the number of methylene groups and ether oxygen atoms, respectively). Values of Π_o are -1.17, -1.13_1, and -1.16_9 for 12C4, 15C5, and 18C6, respectively. They are almost the same. The Π_o value is -1.16 on the average. It can be seen from Π_{CH_2} and Π_o values that a methylene group is lipophilic, whereas an ether oxygen atom is hydrophilic. Values of $\log K_D(L)$ at 25 °C of crown ethers between benzene and water, which are unknown, can be estimated from these empirical parameters.

In a similar manner as above, the contribution of an ether oxygen atom to $\Delta H_D(L)$ ($\Delta H_D(o)$) and $\Delta S_D(L)$ ($\Delta S_D(o)$) between benzene and water was calculated from $\Delta H_D(L)$ and $\Delta S_D(L)$ of 15C5 ($20._9$ kJ mol^{-1} and $53._9$ J K^{-1} mol^{-1}, respectively[10]) and 18C6 by use of $\Delta H_{ex,ip}(CH_2)$ and $\Delta S_{ex,ip}(CH_2)$ determined in this study ($\Delta H_D(o)=(\Delta H_D(L)-\Delta H_{ex,ip}(CH_2)\times a)\div b$, $\Delta S_D(o)=(\Delta S_D(L)-\Delta S_{ex,ip}(CH_2)\times a)\div b$). Values of $\Delta H_D(o)$ and $\Delta S_D(o)$ are 1.7 kJ mol^{-1} and -16 J K^{-1} mol^{-1} for 15C5, and 3.8 kJ mol^{-1} and -10 J K^{-1} mol^{-1} for 18C6, respectively. They are roughly equal. Values of $\Delta H_D(o)$ and $\Delta S_D(o)$ are 2.8 kJ mol^{-1} and -13 J K^{-1} mol^{-1} on the average, respectively. Positive $\Delta H_D(o)$ value and negative $\Delta S_D(o)$ value seem to reflect the interaction between the ether oxygen atom and water. The strong interaction of an ether oxygen atom with water has been reported.[11] By using these empirical thermodynamic parameters, $\Delta H_D(L)$ and $\Delta S_D(L)$ of crown ethers between benzene and water can be roughly estimated.

Transfer process of 18C6 from water to benzene is endothermic, and the ΔS_{D}(18C6) value between benzene and water is positive. Favorable $T\Delta S_{\mathrm{D}}$(18C6) value at 25 °C for transfer of 18C6 from water to benzene is completely canceled by larger unfavorable ΔH_{D}(18C6) value, resulting in relatively large negative log K_{D}(18C6) value. A similar tendency is observed for partition of 15C5 itself between benzene and water.[10]

Extraction of Alkali Metal Picrates with 18C6. Table 2 shows that both ΔH_{ex} and ΔS_{ex} values of 18C6 for all the alkali metals are negative. The same trend is observed for 15C5,[10] benzo-15-crown-5,[12] and dibenzo-18-crown-6[13] between benzene and water, and for 15C5[14] and 18C6[15] between $CHCl_3$ and water. Differences in ΔH_{ex} values among K, Rb, and Cs are small, whereas ΔH_{ex} value of Na is much larger than the others. The same is true for $T\Delta S_{\mathrm{ex}}$ values. The smallest ΔH_{ex} value of K is balanced by the second smallest $T\Delta S_{\mathrm{ex}}$ value, leading to the largest log K_{ex}, and much the greatest ΔH_{ex} and $T\Delta S_{\mathrm{ex}}$ values of Na compensate each other, resulting in the smallest log K_{ex}. Values of ΔH_{D}(18C6) and ΔS_{D}(18C6) play a major role in determining the magnitude of ΔH_{ex} and ΔS_{ex} values, respectively, whereas ΔH_{ML}, $\Delta H_{\mathrm{ex,ip}}$, ΔS_{ML}, and $\Delta S_{\mathrm{ex,ip}}$ values play a minor role.

Ion-Pair Extraction of Crown Ether-Alkali Metal Ion Complexes with Picrate Anions. Ion-pair extractability at 25 °C of M(18C6)A between benzene and water increases in the order, Na<Cs<Rb<K (Table 2). Much the largest $\Delta H_{\mathrm{ex,ip}}$ and $\Delta S_{\mathrm{ex,ip}}$ values of Na compensate each other, resulting in the lowest ion-pair extractability (Table 2). Ion-pair extraction of K(18C6)A and Cs(18C6)A is completely enthalpy controlled. The smallest $\Delta H_{\mathrm{ex,ip}}$ and $\Delta S_{\mathrm{ex,ip}}$ values of Rb balance each other, leading to the second greatest ion-pair extractability.

As can be seen from Table 2, both $\Delta H_{\mathrm{ex,ip}}$ and $\Delta S_{\mathrm{ex,ip}}$ values vary fairly with the alkali metal ion. This may reflect differences in interactions of 18C6–alkali metal ion complexes with picrate anions in an aqueous phase and water molecules.

Values[15] of log $K_{\mathrm{ex,ip}}$, $\Delta H_{\mathrm{ex,ip}}$, and $T\Delta S_{\mathrm{ex,ip}}$ of 18C6–alkali metal picrate complexes between $CHCl_3$ and water are as follows.

	Na	K	Rb	Cs
log($K_{\mathrm{ex,ip}}$/mol^{-1} dm^3) (at 25°C)	3.46	4.83	4.88	4.42
$\Delta H^{\circ}_{\mathrm{ex,ip}}$/kJ mol^{-1}	$-18._8$	$-33._9$	$-45._6$	$-43._1$
$T\Delta S^{\circ}_{\mathrm{ex,ip}}$/kJ mol^{-1} (at 25°C)	0.6	$-6._6$	$-17._8$	$-18._1$

Log $K_{\mathrm{ex,ip}}$(MLA) value of the $CHCl_3/H_2O$ system is about 2 larger than that of the benzene/H_2O system. The difference in log $K_{\mathrm{ex,ip}}$(MLA) values between $CHCl_3$ and benzene systems (ca. 2) is smaller than that in individual extraction constants for solvents between $CHCl_3$ and benzene (3.4—4.2).[16] It is impossible to explain the large difference at the present time.

Both $\Delta H_{\mathrm{ex,ip}}$ and $\Delta S_{\mathrm{ex,ip}}$ of the 18C6–alkali metal picrate complex increase very much from $CHCl_3$ to benzene. This indicates that the interaction of the 18C6–alkali metal picrate complex with $CHCl_3$ is much stronger than that with benzene. It thus appears that ion-pair of the 16C6–alkali metal ion complex with picrate anion is extracted into $CHCl_3$ much more than into benzene.

Differences in $\Delta H_{\mathrm{ex,ip}}$ and $\Delta S_{\mathrm{ex,ip}}$ values of the 18C6–alkali metal picrate complex between benzene and $CHCl_3$ ($\Delta(\Delta H_{\mathrm{ex,ip}})$ and $\Delta(\Delta S_{\mathrm{ex,ip}})$) express enthalpy and entropy change of transfer of the 18C6 complex, respectively, from benzene (or $CHCl_3$) to $CHCl_3$ (or benzene). A large difference in $\Delta(\Delta H_{\mathrm{ex,ip}})$ values of 18C6 complexes is found between a group of Na and Cs and that of K and Rb. The same is true for $\Delta(\Delta S_{\mathrm{ex,ip}})$ values. This may reflect the difference in solute-solvent interactions caused by the difference in structures of the 18C6–alkali metal picrate complexes; namely, K^+ and Rb^+ have more suitable sizes for the 18C6 cavity than Na^+ and Cs^+.

Values[10] of log $K_{\mathrm{ex,ip}}$, $\Delta H_{\mathrm{ex,ip}}$, and $T\Delta S_{\mathrm{ex,ip}}$ of 15C5–sodium picrate complex between benzene and water are 2.40 (at 25 °C), $-18._1$ kJ mol^{-1}, and $-4._6$ kJ mol^{-1} (at 25 °C), respectively. Since Na^+ and K^+ fit most nicely into 15C5 and 18C6 cavity, respectively, the metal ion trapped in the cavity is most effectively screened by the crown ether from environmental solvents. A nitrogen atom of tetraalkylammonium ion is well-shielded by four alkyl groups. Sizes of n-Pr_4N^+ and n-Bu_4N^+ ions are nearly equal to those of 15C5–Na^+ and 18C6–K^+ complexes, respectively.[17] Thus, it is interesting to compare the ion-pair-extraction process of 15C5–NaA and 18C6–KA complexes with that of n-Pr_4NA and n-Bu_4NA, respectively, from a thermodynamic point of view. A striking difference is found between the crown ether complexes and the tetraalkylammonium picrates. Values of $\Delta H_{\mathrm{ex,ip}}$ and $\Delta S_{\mathrm{ex,ip}}$ of 15C5–NaA and 18C6–KA complexes except for $\Delta S_{\mathrm{ex,ip}}$ value of the 18C6–KA complex are negative, and $\Delta S_{\mathrm{ex,ip}}$ value of the 18C6–KA complex is nearly equal to zero (Table 2). On the contrary, all the $\Delta H_{\mathrm{ex,ip}}$ and $\Delta S_{\mathrm{ex,ip}}$ values of n-Pr_4NA and n-Bu_4NA are positive. Values of $\Delta H_{\mathrm{ex,ip}}$ and $\Delta S_{\mathrm{ex,ip}}$ of the crown ether complex (18C6–KA, 15C5–NaA) are much smaller than those of the corresponding R_4NA (n-Bu_4NA, n-Pr_4NA). Ion-pair extraction of the crown ether complexes is enthalpy controlled, whereas, that of n-Pr_4NA and n-Bu_4NA is entropy controlled. Ion-pair extractability at 25 °C of the 18C6–KA complex is lower than that of n-Bu_4NA, and the contrary holds for the 15C5–NaA complex and n-Pr_4NA. From the above discussion and the fact that both n-Pr_4N^+ and n-Bu_4N^+ are structure makers in an aqueous solution,[8] it may be concluded that both

18C6-K^+ and 15C5-Na^+ complexes act as a structure breaker in water. In a series of our conductance studies,[5,18-20] it was reported that the 18C6-K^+ complex acts as a structure breaker in protic solvents. The result of this study for the 18C6-K^+ complex agrees with that of conductometry.

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$$K_{\mathrm{Ph_4As^+}}=K_{\mathrm{Ph_4B^-}},\ K_{\mathrm{benzene}}=1.0.$$

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