Solvent Effects on Extraction of Sodium Picrate with 15-Crown-5. The Determination of Ion-Pair Formation Constant of Crown Ether–Metal Salt 1 : 1 : 1 Complex in Water

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In order to determine the ion-pair formation constant of a crown ether–metal salt complex (1 : 1 : 1) in water, an equation is derived from the regular solution theory. Then, the theoretical predictions are verified experimentally by solvent extraction with 15-crown-5 (15C5), sodium picrate (NaA), and various organic solvents of low dielectric constant. The partition constants of 15C5 and the actual overall extraction constants of NaA with 15C5 were determined at 25±0.2 °C. The partition constants of the Na(15C5)A complex are calculated from these data, the literature value for the complex-formation constant of $\mathrm{Na(15C5)^+}$ in water, and the ion-pair formation constant ($K_{\mathrm{Na(15C5)A}}$) in water determined in this study ($\log K_{\mathrm{Na(15C5)A}}=4.09\pm0.23$ at 25 °C). The distribution behavior of 15C5 and Na(15C5)A is explained by the regular solution theory. The obtained molar volumes $V/\mathrm{cm^3\,mol^{-1}}$ and solubility parameters $\delta/\mathrm{cal^{1/2}\,cm^{-3/2}}$ are as follows; $V_{\mathrm{15C5}}=189\pm34$, $V_{\mathrm{Na(15C5)A}}=215\pm46$, $\delta_{\mathrm{15C5}}=12.0\pm0.1$, and $\delta_{\mathrm{Na(15C5)A}}=12.0\pm0.1$.

When a metal salt is extracted with a crown ether into an organic solvent of low dielectric constant, the overall extraction equilibrium can be analyzed by four fundamental equilibria; (1) partition of the crown ether, (2) complex formation of the crown ether with the metal ion in water, (3) ion-pair formation of the crown ether complex with the anion in water, and (4) partition of the ion-pair crown ether complex.[1] In most cases, the overall extraction constant and the partition constant of a crown ether can be determined; in some cases, the complex-formation constant in water. The ion-pair formation constant gives a clue to quantitatively study the distribution behavior of the ion-pair crown ether complex as well as provides information on solute–solute and –solvent interactions of the crown ether complex. But it is very difficult to determine ion-pair formation constants of crown ether–metal ion complexes with anions in water because of the low stability of the crown ether–metal ion complexes. Thus, no reliable ion-pair formation constants have been reported. In addition, it is impossible to measure the partition constant of the ion-pair crown ether complex on account of its low stability in water.

This paper presents a more completed method to determine the ion-pair formation constant of the crown ether–metal salt 1 : 1 : 1 complex in water.[2] The theoretical predictions are verified experimentally by solvent extraction with 15-crown-5 (15C5), sodium picrate, and various organic solvents of low dielectric constant. Furthermore, the distribution behavior of 15C5 and the 15C5-sodium picrate 1 : 1 : 1 complex is explained by the regular solution theory.[3]

Experimental

Materials. 15-Crown-5 (Nisso Co., Ltd.) was purified by distillation under vacuum (bp 167—168 °C, 19 mmHg (1 mmHg≈133.322 Pa)). All the organic solvents were analytical grade reagents; 1,1-dichloroethane and 1,2-dichloroethane were purified by distillation, but the others were not purified. They were washed four times with deionized water prior to use. Picric acid and NaOH were of analytical grade.

Distribution Constants of 15C5. A 10 ml portion of an organic solution of 15C5 and an equal volume of deionized water in a stoppered glass tube (volume 30 ml) were shaken in a thermostated water bath for 2 h at 25±0.2 °C and centrifuged. The concentration ranges of 15C5 were 9.0×10^{-6}—2.4×10^{-3} M (1 M=1 mol dm^{-3}) for (I) and (II), and 1.0×10^{-2}—7.5×10^{-1} M for (III).

(I) Except for the 1,1,1-trichloroethane, dichloromethane, and 1,2-dichloroethane systems, a $10-2n$ ml portion of the organic phase and an equal volume of water were placed in a stoppered glass tube (No. n), agitated for 2 h at 35 °C, and centrifuged. This procedure was repeated until $n=2$ or 3. A $5-n$ ml portion of the aqueous phase in the No. n stoppered glass tube, $5+n$ ml portion of an aqueous solution (pH 11.0—11.8) containing NaOH (1.1×10^{-1} M) and picric acid (1.0×10^{-1} M), and 10 ml $\mathrm{CHCl_3}$ were placed in a stoppered glass tube (No. m), shaken for 2 h at 0 °C, and centrifuged. In order to complete the complexation with $\mathrm{Na^+}$ of uncomplexed 15C5 in the $\mathrm{CHCl_3}$ phase in the No. m stoppered glass tube, a 8 ml portion of the $\mathrm{CHCl_3}$ phase and an equal volume of an aqueous solution (pH 11.0—11.8) containing NaOH (1.1×10^{-1} M) and picric acid (1.0×10^{-1} M) were placed in a stoppered glass tube, agitated for 2 h at 0 °C, and centrifuged. No increased picrate extraction into the $\mathrm{CHCl_3}$ phase was observed. A $10-2m$ ml portion of the aqueous phase in the No. m stoppered glass tube and an equal volume of $\mathrm{CHCl_3}$ were placed in a stoppered glass tube (No. ($m+1$)), shaken for 2 h at 0 °C, and centrifuged. This procedure was repeated until $m=2$ or 3. The picrate extracted into the respective $\mathrm{CHCl_3}$ phases was back extracted into 0.01 M NaOH aqueous solution (volume ratio 1 : 1), and the picrate concentration was determined spectrophotometrically ($\lambda_{\max}=356$ nm, $\varepsilon=1.44\times10^4$ cm^{-1} M^{-1}). The concentration of the 15C5 which distributed into the 10 ml organic phase was calculated from the total concentration of the extracted 15C5-sodium picrate complex in a series of these extractions.

(II) For the dichloromethane and 1,2-dichloroethane systems, the concentration of the 15C5 which distributed into the 10 ml water was determined in the same way as described in the preceding section (I) except for the process for the back extraction into water of the 15C5 in the organic phase.

(III) For the 1,1,1-trichloroethane system, a 8 ml portion of the organic phase was transferred to a 10 ml beaker, left for several days until evaporation was complete, and the residue weighed.

The partition constants of 15C5 are listed in Table 1.

Extraction of Sodium Picrate with 15C5. A 10—13 ml portion of an organic solution of 15C5 (1.8×10^{-5}—1.5×10^{-2} M) and an equal volume of an aqueous solution of NaOH (4.8×10^{-3}—4.1×10^{-2} M) and picric acid (2.8×10^{-4}—4.7×10^{-3} M) in a stoppered glass tube were shaken in a thermostated water bath at 25±0.2 °C for 2 h and centrifuged. Extractions were performed at pH 10.8—11.9. Except for the cases of *o*-dichlorobenzene, chlorobenzene, and bromobenzene, a 8—11 ml portion of the organic phase was transferred to a 50 ml beaker and left for several days until evaporation was complete. The residue was dissolved in 0.01 M NaOH aqueous solution and the picrate concentration was determined spectrophotometrically at 356 nm. In the cases of *o*-dichlorobenzene, chlorobenzene, and bromobenzene, the picrate in the organic phase was back extracted into 0.01 M NaOH aqueous solution, and the picrate concentration was determined by spectrophotometry.

Theory and Results

When an equilibrium is established between an aqueous phase of sodium picrate (NaA) and an organic phase of 15C5 (L), the equilibrium constants are defined as

$$K_{\mathrm{ex}} = [\mathrm{NaLA}]_{\mathrm{o}}/[\mathrm{Na}^+][\mathrm{L}]_{\mathrm{o}}[\mathrm{A}^-], \tag{1}$$

$$K_{\mathrm{D,L}} = [\mathrm{L}]_{\mathrm{o}}/[\mathrm{L}], \tag{2}$$

$$K_{\mathrm{ML}} = [\mathrm{NaL}^+]/[\mathrm{Na}^+][\mathrm{L}] \quad (K_{\mathrm{ML}} = 5.0 \text{ at } 25\ ^\circ\mathrm{C}^{4)}), \tag{3}$$

$$K_{\mathrm{MLA}} = [\mathrm{NaLA}]/[\mathrm{NaL}^+][\mathrm{A}^-], \tag{4}$$

$$K_{\mathrm{D,MLA}} = [\mathrm{NaLA}]_{\mathrm{o}}/[\mathrm{NaLA}], \tag{5}$$

where the subscript "o" and the lack of subscript denote the organic and the aqueous phase, respectively. From the low dielectric constants (ε_{r}) of the diluents used in this study, it has been assumed that the dissociation of NaLA into NaL^+ and A^- in the organic phases is negligible. The overall extraction equilibrium constant (K_{ex}) can be written as

$$K_{\mathrm{ex}} = K_{\mathrm{D,L}}{}^{-1}K_{\mathrm{ML}}K_{\mathrm{MLA}}K_{\mathrm{D,MLA}}. \tag{6}$$

The distribution ratio (D) of sodium is represented by

$$D = [\mathrm{NaLA}]_{\mathrm{o}}/([\mathrm{Na}^+] + [\mathrm{NaL}^+] + [\mathrm{NaLA}]). \tag{7}$$

In the case of $[\mathrm{Na}^+]\gg[\mathrm{NaL}^+]+[\mathrm{NaLA}]$, Eq. 7 is transformed into

$$D = K_{\mathrm{ex}}[\mathrm{L}]_{\mathrm{o}}[\mathrm{A}^-]. \tag{8}$$

From the mass balances, $[\mathrm{Na}^+]$, $[\mathrm{L}]_{\mathrm{o}}$, and $[\mathrm{A}^-]$ are given by

$$\begin{aligned}[\mathrm{Na}^+] = {} & ([\mathrm{Na}]_{\mathrm{t}} - [\mathrm{NaLA}]_{\mathrm{o}})/(1 + K_{\mathrm{ML}}K_{\mathrm{D,L}}{}^{-1}[\mathrm{L}]_{\mathrm{o}} \\ & + K_{\mathrm{ML}}K_{\mathrm{D,L}}{}^{-1}K_{\mathrm{MLA}}[\mathrm{L}]_{\mathrm{o}}[\mathrm{A}^-]),\end{aligned} \tag{9}$$

$$\begin{aligned}[\mathrm{L}]_{\mathrm{o}} = {} & ([\mathrm{L}]_{\mathrm{t}} - [\mathrm{NaLA}]_{\mathrm{o}})/(1 + K_{\mathrm{D,L}}{}^{-1} + K_{\mathrm{ML}}K_{\mathrm{D,L}}{}^{-1}[\mathrm{Na}^+] \\ & + K_{\mathrm{ML}}K_{\mathrm{D,L}}{}^{-1}K_{\mathrm{MLA}}[\mathrm{Na}^+][\mathrm{A}^-]),\end{aligned} \tag{10}$$

$$\begin{aligned}[\mathrm{A}^-] = {} & ([\mathrm{HA}]_{\mathrm{t}} - [\mathrm{NaLA}]_{\mathrm{o}})/\{1 + (K_{\mathrm{HA}} + K_{\mathrm{ex}}(\mathrm{HA}))[\mathrm{H}^+] \\ & + K_{\mathrm{ML}}K_{\mathrm{D,L}}{}^{-1}K_{\mathrm{MLA}}[\mathrm{Na}^+][\mathrm{L}]_{\mathrm{o}}\},\end{aligned} \tag{11}$$

where $K_{\mathrm{HA}} = [\mathrm{HA}]/[\mathrm{H}^+][\mathrm{A}^-]$, $K_{\mathrm{ex}}(\mathrm{HA}) = [\mathrm{HA}]_{\mathrm{o}}/[\mathrm{H}^+][\mathrm{A}^-]$, and the subscript "t" denotes the total concentration. As a first approximation, it is assumed that $1\gg K_{\mathrm{ML}}K_{\mathrm{D,L}}{}^{-1}[\mathrm{L}]_{\mathrm{o}}+K_{\mathrm{ML}}K_{\mathrm{D,L}}{}^{-1}K_{\mathrm{MLA}}[\mathrm{L}]_{\mathrm{o}}[\mathrm{A}^-]$ (Eq. 9), $1+K_{\mathrm{D,L}}{}^{-1}+K_{\mathrm{ML}}K_{\mathrm{D,L}}{}^{-1}[\mathrm{Na}^+]\gg K_{\mathrm{ML}}K_{\mathrm{D,L}}{}^{-1}K_{\mathrm{MLA}}[\mathrm{Na}^+][\mathrm{A}^-]$ (Eq. 10), and $1\gg(K_{\mathrm{HA}}+K_{\mathrm{ex}}(\mathrm{HA}))[\mathrm{H}^+]+K_{\mathrm{ML}}K_{\mathrm{D,L}}{}^{-1}K_{\mathrm{MLA}}[\mathrm{Na}^+][\mathrm{L}]_{\mathrm{o}}$ (Eq. 11) under these experimental conditions. For Eq. 8, the $[\mathrm{L}]_{\mathrm{o}}$ and $[\mathrm{A}^-]$ values were calculated on the basis of this assumption. Plots of $\log(D/[\mathrm{A}^-])$ vs. $\log[\mathrm{L}]_{\mathrm{o}}$ always give a straight line with a slope of 1 in every case. This indicates that the 15C5 forms a 1:1 complex with the Na^+ ion and that the above assumptions are valid. The first approximate K_{ex} value of each system was determined based on the assumptions.

The distribution constant ($K_{\mathrm{D,L}}$) of 15C5 is estimated by the following equation derived from the regular solution theory.[3)]

$$RT\ \ln K_{\mathrm{D,L}}/(\delta_{\mathrm{w}} - \delta_{\mathrm{o}}) = V_{\mathrm{L}}(\delta_{\mathrm{w}} - 2\delta_{\mathrm{L}}) + V_{\mathrm{L}}\delta_{\mathrm{o}}' \tag{12}$$

where $\delta_{\mathrm{o}}'=\delta_{\mathrm{o}}+RT(1/V_{\mathrm{o}}-1/V_{\mathrm{w}})/(\delta_{\mathrm{w}}-\delta_{\mathrm{o}})$; δ_{w}, δ_{o}, and δ_{L} denote the solubility parameters of water, the organic solvent, and 15C5, respectively; V_{L}, V_{o}, and V_{w} the molar volume of 15C5, the organic solvent, and water, respectively. The distribution constant ($K_{\mathrm{D,MLA}}$) of a neutral ion-pair complex NaLA is estimated by Eq. 13.

$$RT\ \ln K_{\mathrm{D,MLA}}/(\delta_{\mathrm{w}} - \delta_{\mathrm{o}}) = V_{\mathrm{MLA}}(\delta_{\mathrm{w}} - 2\delta_{\mathrm{MLA}}) + V_{\mathrm{MLA}}\delta_{\mathrm{o}}' \tag{13}$$

where V_{MLA} and δ_{MLA} designate the molar volume and solubility parameter of NaLA, respectively. Combination of Eqs. 12 and 13 leads to Eq. 14.

$$\begin{aligned}\log K_{\mathrm{D,MLA}} = {} & \{V_{\mathrm{MLA}}(\delta_{\mathrm{w}} + \delta_{\mathrm{o}}' - 2\delta_{\mathrm{MLA}}) \\ & /V_{\mathrm{L}}(\delta_{\mathrm{w}} + \delta_{\mathrm{o}}' - 2\delta_{\mathrm{L}})\}\log K_{\mathrm{D,L}}\end{aligned} \tag{14}$$

Equation 15 is obtained by adding $\log K_{\mathrm{MLA}}$ to both sides of Eq. 14.

$$\begin{aligned}\log K_{\mathrm{ex,ip}} = {} & \{V_{\mathrm{MLA}}(\delta_{\mathrm{w}} + \delta_{\mathrm{o}}' - 2\delta_{\mathrm{MLA}}) \\ & /V_{\mathrm{L}}(\delta_{\mathrm{w}} + \delta_{\mathrm{o}}' - 2\delta_{\mathrm{L}})\}\log K_{\mathrm{D,L}} + \log K_{\mathrm{MLA}}\end{aligned} \tag{15}$$

where $K_{\mathrm{ex,ip}} = [\mathrm{NaLA}]_{\mathrm{o}}/[\mathrm{NaL}^+][\mathrm{A}^-] = K_{\mathrm{MLA}}K_{\mathrm{D,MLA}}$. The first approximate $\log K_{\mathrm{MLA}}$ value can be obtained from the intercept of the plots of $\log K_{\mathrm{ex,ip}}$ (first approximate values) vs. $\log K_{\mathrm{D,L}}$ (Fig. 1). Using the first approximate values of $[\mathrm{Na}^+]$, $[\mathrm{L}]_{\mathrm{o}}$, and K_{MLA}, the second approximate $[\mathrm{A}^-]$ value is calculated from Eq. 16.

Table 1. Equilibrium Constants and Solvent Parameters at 25 °C

No.	Solvent	$K_{D,L}$ a)	$\log K_{ex}$ a)	$\log K_{ex,ip}$ b)	δ c)	V d)	E_T e)	ε_r f)
1	CH_2Cl_2 (DCM)	4.40 ± 0.03	4.623 ± 0.004	4.57	9.7	63.9	41.1	8.93
2	$CHCl_3$ (CF)	8.2_7 g)	4.019 ± 0.004	4.24	9.3	80.7	39.1	4.81 h)
3	CCl_4 (CTC)	$(6.24\pm0.15)\times10^{-2}$	—	—	8.6	97.1	32.5	2.24 h)
4	CH_3CHCl_2 (1,1-DCE)	$(4.04\pm0.14)\times10^{-1}$	5.11 ± 0.01	4.02	9.1	85	—	10.0 i)
5	CH_2ClCH_2Cl (1,2-DCE)	1.04 ± 0.03	4.70 ± 0.03	4.02	9.8	79.4	41.9	10.36
6	CH_3CCl_3 (1,1,1-TCE)	$(1.41\pm0.11)\times10^{-1}$	—	—	8.5	100	—	7.53 h)
7	$CH_3(CH_2)_3Cl$ (CBu)	$(6.32\pm0.08)\times10^{-2}$	4.722 ± 0.008	2.82	8.4	104	—	7.39 h)
8	C_6H_6 (BZ)	$1.5_6\times10^{-1}$ 9)	4.67 ± 0.01	3.15	9.16	89.4	34.5	2.275
9	$C_6H_5CH_3$ (TE)	$(7.12\pm0.10)\times10^{-2}$	4.750 ± 0.007	2.90	8.93	106.9	33.9	2.379
10	m-$C_6H_4(CH_3)_2$ (mX)	$(4.28\pm0.16)\times10^{-2}$	4.76 ± 0.01	2.70	8.88	123.5	—	2.4
11	C_6H_5Cl (CB)	$(1.79\pm0.06)\times10^{-1}$	5.21 ± 0.02	3.77	9.5	102.1	37.5	5.62
12	C_6H_5Br (BB)	$(3.57\pm0.07)\times10^{-1}$	4.61 ± 0.01	3.46	9.87	105	37.5	5.40
13	o-$C_6H_4Cl_2$ (o-DCB)	$(3.19\pm0.07)\times10^{-1}$	5.071 ± 0.008	3.88	10.0	112.8	—	9.93
14	H_2O	—	—	—	17.55 j)	18.1	—	—

a) Each equilibrium-constant value is the average of 13—22 measurements. The uncertainties are the standard deviations. b) The $K_{ex,ip}$ value was calculated by Eq. 6. c) Solubility parameter ($cal^{1/2}\ cm^{-3/2}$). Ref. 3. A. F. M. Barton, *Chem. Rev.*, **75**, 731 (1975). d) Molar volume ($cm^3\ mol^{-1}$). R. C. Weast, "Handbook of Chemistry and Physics," 58th ed, CRC Press, Ohio (1977—1978) (density). e) Transition energy ($kcal\ mol^{-1}$). C. Reichard and K. Dimroth, *Fortschr. Chem. Forsch.*, **11**, 1 (1968). f) J. A. Riddick and W. B. Bunger, "Organic Solvents," 3rd ed, Wiley-Interscience, New York (1970). g) Y. Takeda, N. Ikeo, and N. Sakata, *Talanta*, **38**, 1325 (1991). h) 20 °C. i) 18 °C. j) T. Omori, T. Wakahayashi, S. Oki, and N. Suzuki, *J. Inorg. Nucl. Chem.*, **26**, 2265 (1964).

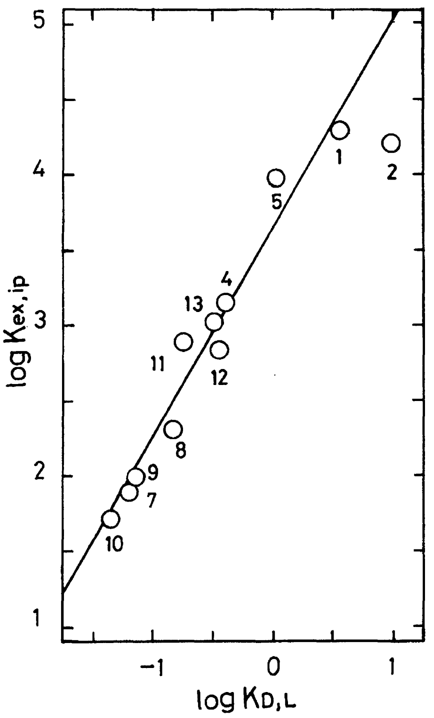

Fig. 1. Plots of first approximate $\log K_{ex,ip}$ values vs. $\log K_{D,L}$ values for 15C5. The numbers correspond to those in Table 1.

$$[A^-] = ([HA]_t - [NaLA]_o)/(1 + K_{ML}K_{D,L}{}^{-1}K_{MLA}[Na^+][L]_o) \tag{16}$$

Thus, the actual $[Na^+]$, $[L]_o$, $[A^-]$, K_{MLA}, and K_{ex} values are calculated from Eqs. 1, 6, 9, 10, 15, and 16 by a successive approximation method. The $\log K_{MLA}$ value is 4.09 ± 0.23. The actual $\log K_{ex}$ and $\log K_{ex,ip}$ values are summarized in Table 1. The plots of the actual $\log K_{ex,ip}$ values vs. $\log K_{D,L}$ values in Fig. 2 show a good linear relationship (the correlation coefficient r=0.935) except for CF. It is very difficult to measure the K_{MLA} values of crown ether–metal salt complexes in water because of the low stability of the crown ether–metal ion complexes in water. But, the K_{MLA} values can be obtained by this method.

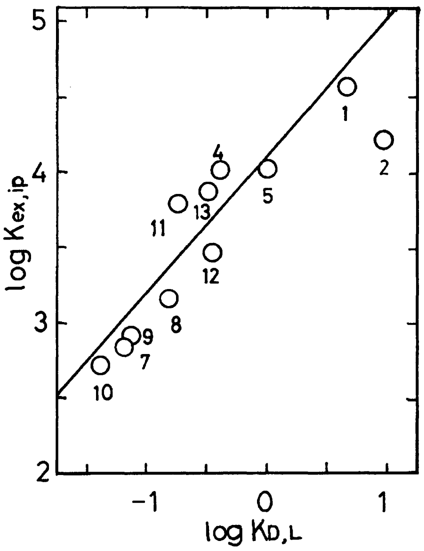

Fig. 2. Plots of actual $\log K_{ex,ip}$ values vs. $\log K_{D,L}$ values for 15C5. The numbers correspond to those in Table 1.

Discussion

$RT\ln K_{D,L}/(\delta_w-\delta_o)$ vs. $\delta_o{}'$ plots for 15C5 in Fig. 3 show a linear relationship except for CF. A similar large positive deviation of CF has been reported on the

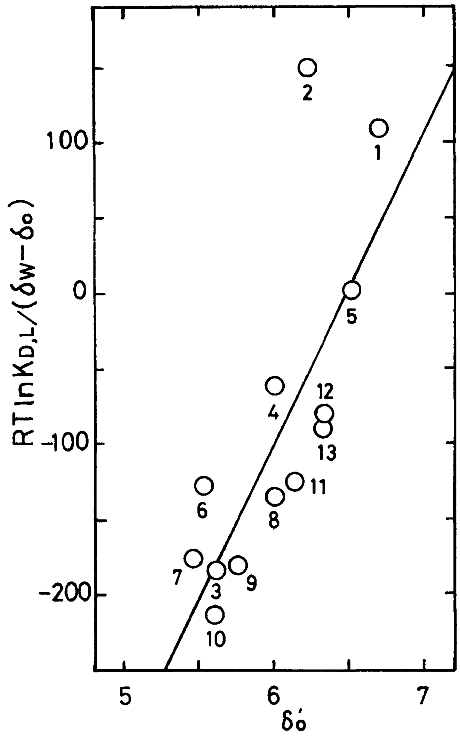

Fig. 3. $RT \ln K_{\mathrm{D,L}}/(\delta_{\mathrm{w}}-\delta_{\mathrm{o}})$ vs. δ_{o}' plots when L=15C5. The numbers correspond to those in Table 1.

18-crown-6 (18C6) system.[5] This is attributable to the hydrogen bond between the crown ether and CF. The V and δ values of 15C5 are calculated from the slope and the intercept to be 189±34 and 12.0±0.1, respectively. The experimental $V_{15\mathrm{C}5}$ value agrees well with that (205 $\mathrm{cm}^3\,\mathrm{mol}^{-1}$) calculated from group contributions according to Bondi.[6] Although 15C5 is smaller in size than 18C6, the lipophilicity of 15C5 is higher than that of 18C6.[7] This is due to the smaller δ_{L} value of 15C5 compared with 18C6 ($\delta_{18\mathrm{C}6}=12.9$ $\mathrm{cal}^{1/2}\,\mathrm{cm}^{-3/2}$ [5])).

The $\log K_{\mathrm{D,NaLA}}$ values calculated from the $\log K_{\mathrm{ex,ip}}$ and $\log K_{\mathrm{NaLA}}$ values are listed in Table 2. Although the neutral Na(15C5)A complex is bulky, it is rather hydrophilic.

Table 2. $\log K_{\mathrm{D,NaLA}}$ Values for 15C5 at 25 °C

No.	Solvent	$\log K_{\mathrm{D,NaLA}}$
1	DCM	0.47
2	CF	0.14
3	CTC	—
4	1,1-DCE	−0.08
5	1,2-DCE	−0.08
6	1,1,1-TCE	—
7	CBu	−1.28
8	BZ	−0.95
9	TE	−1.20
10	*m*X	−1.40
11	CB	−0.33
12	BB	−0.64
13	*o*-DCB	−0.23

For the ion-pair complex Na(15C5)A, a linear relationship is found between $RT \ln K_{\mathrm{D,NaLA}}/(\delta_{\mathrm{w}}-\delta_{\mathrm{o}})$ and δ_{o}' in Fig. 4. The abnormal behavior of CF which is shown in Fig. 3 is not observed in Fig. 4. This indicates that hydrogen bonding of CF to ether oxygen atoms of

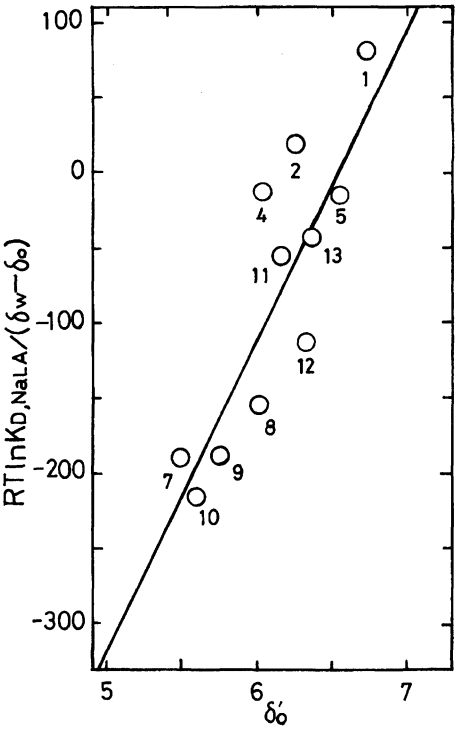

Fig. 4. $RT \ln K_{\mathrm{D,NaLA}}/(\delta_{\mathrm{w}}-\delta_{\mathrm{o}})$ vs. δ_{o}' plots when L=15C5. The numbers correspond to those in Table 1.

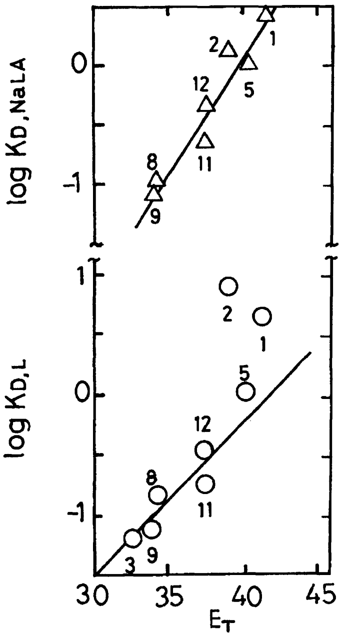

Fig. 5. $\log K_{\mathrm{D,L}}$ and $\log K_{\mathrm{D,NaLA}}$ vs. E_{T} plots when L=15C5. The numbers correspond to those in Table 1.

15C5 when 15C5 is complexed is greatly decreased as a result of ionic Na^+–O bonding.$^{10)}$

The V and δ values of Na(15C5)A were determined to be 215±46 and 12.0±0.1 from the slope and the intercept of the straight line in Fig. 4, respectively. The $V_{\mathrm{NaLA}}/V_{\mathrm{L}}$ value, 1.1_3, of 15C5 is nearly equal to the slope, 0.95, of the straight line of the $\log K_{\mathrm{ex,ip}}$ vs. $\log K_{\mathrm{D,L}}$ plots in Fig. 2. The δ_{NaLA} and δ_{L} values are identical. The V_{NaLA} value is larger than the V_{L} value. But, except for the cases of 1,1-DCE, CB, and *o*-DCB, the $\log K_{\mathrm{D,NaLA}}$ value is smaller than or nearly equal to the $\log K_{\mathrm{D,L}}$ value. Except for the CF system, this may be attributed to the small difference between V_{NaLA} and V_{L} values and the errors inherent in the solvent extraction. For the CF system, the hydrogen bond between 15C5 and CF is responsible for the unexpectedly greater $\log K_{\mathrm{D,L}}$ value than the $\log K_{\mathrm{D,NaLA}}$ value.

The plots of $\log K_{\mathrm{D,L}}$ and $\log K_{\mathrm{D,NaLA}}$ against E_{T} for the organic solvents are given in Fig. 5. A better linear relationship is observed for the $\log K_{\mathrm{D,L}}$ and $\log K_{\mathrm{D,NaLA}}$ vs. E_{T} plots. In the former case, CF and DCM deviate far from the straight line.

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7) $\log K_{\mathrm{D,L}}$ values of 18C6 at 25 °C; 0.78_6 (CF),$^{8)}$ 0.60 (DCM),$^{5)}$ 0.05 (1,2-DCE),$^{5)}$ −0.90 (CB),$^{5)}$ -1.19_7 (BZ),$^{9)}$ −1.62 (TE),$^{5)}$ and −1.80 (*m*X).$^{5)}$

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