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Crown Ether Complexed Alkali Metal Picrate Ion Pairs in Water-Saturated Dichloromethane As Studied by Electrolytic Conductance and by Partitioning into Water. Effect of Lithium Chloride on Partitioning

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The equilibrium constant of extraction of lithium, sodium, or potassium picrates, MPi, with 18-crown-6 or dibenzo-18-crown-6 between water and dichloromethane was determined spectrophotometrically and compared with literature values. In all instances, a 1:1:1 complex was extracted. The value of the ionic association constant of the complexed potassium picrate in the organic phase agrees well with that from electrolytic conductivity data. The latter reveals the presence of both cationic and anionic ion triplets in solutions $>3 \times 10^{-3}$ mol^{-1} dm^{-3}. The effect of temperature on the solubility of dibenzo-18-crown-6 in water saturated with dichloromethane yields $\Delta H = -16.4$ kJ mol^{-1} and $\Delta S = -36.0_2$ kJ mol^{-1} K^{-1}. Values of the activity coefficient of dibenzo-18-crown-6 at 298.1 K ("salting out effect") in aqueous lithium chloride (0.10 to 0.25 mol dm^{-3}) were estimated from the effect of the salt on the solubility, while the activity coefficient of the crown ether in dichloromethane saturated with water was evaluated from the effect of the salt on the partition coefficient. An estimate of the activity coefficient product, $y(K^+)y(Pi^-)$, in the aqueous lithium chloride solutions was made from the effect of this electrolyte on the extraction constant.

Introduction

Extensive literature dealing with solvent extraction of crown ether complexed alkali metal picrates, LMPi, from water into slightly miscible organic solvents of low polarity, e.g. dichloromethane, is available (Frensdorff, 1971; Inoue *et al.*, 1990; Sekine *et al.*, 1978). Here, L denotes the crown ether and MPi, the alkali metal picrate. When LMPi dissociates to a moderate extent in the organic solvent into LM$^+$ and Pi$^-$ (eq 1)

$$K_A(\mathrm{LMPi}) = a(\mathrm{LMPi})/a(\mathrm{LM}^+)a(\mathrm{Pi}^-) \qquad (1)$$

and the complexation constant, $K(\mathrm{LM}^+)$ (eq 2), is large

$$K(\mathrm{LM}^+) = a(\mathrm{LM}^+)/a(\mathrm{L})a(\mathrm{M}^+) \qquad (2)$$

the value of $K_A(\mathrm{LMPi})$ and the thermodynamic extraction constant, K_{ex} (eq 3), were estimated using a two-parameter regression procedure (Frensdorff, 1971) assuming $y(\mathrm{LMPi})_o = y(\mathrm{L})_o$.

$$K_{ex} = a(\mathrm{LMPi})_o/a(\mathrm{L})_o a(\mathrm{M}^+)_w a(\mathrm{Pi}^-)_w = K^c_{ex} y(\mathrm{LMPi})_o/y(\mathrm{L})_o y(\mathrm{M}^+)_w y(\mathrm{Pi}^-)_w \qquad (3)$$

The symbol *y* denotes the activity coefficient, the superscript c denotes the concentration equilibrium constant, and the lack of superscript refers to the thermodynamic constant, while the subscripts o and w denote the organic and aqueous phase, respectively.

Alternatively, $K_A(\mathrm{LMPi})$ can be evaluated from electrolytic conductivity data in dilute solutions of MPi in the presence of an excess of crown ether (Kolthoff *et al.*, 1993). In this paper, values of $K_A(\mathrm{LMPi})$ from the two methods are compared for KPi complexes with 18-crown-6 (18-cr-6) or dibenzo-18-crown-6 (DB-18-cr-6) in DCM(W). Beronius and Brändström (1976) found good agreement in K_A from conductance and partitioning of tetraalkylammonium picrates between W(DCM) and DCM(W). Dichloromethane saturated with water and water saturated with dichloromethane are abbreviated DCM(W) and W(DCM), respectively.

In a review article, Brändström (1982) discusses the influence of higher aggregates (e.g. ion triplets) on partitioning. In this context, it well may be useful to employ differential vapor osmometry (which counts the number of particles present) in a solution of LMPi in pure dichloromethane.

In solvents of higher dielectric permittivity, such as in acetonitrile, LMPi can be considered as completely dissociated and $K(\mathrm{LM}^+)$ estimated conductometrically when the ion mobilities of M$^+$ and LM$^+$ differ appreciably (Evans *et al.*, 1972; Høiland *et al.*, 1979; Takeda, 1983). Large values of $K(\mathrm{LM}^+)$ in solvents of low permittivity can be traced to the large positive free energy of transfer of M$^+$ from solvents of high permittivity (Kolthoff *et al.*, 1993).

Literature data dealing with solution activity coefficients of undissociated LMPi in the organic phase and of L in both phases is lacking. In this study, $y(\mathrm{L})_w$ is found from the effect of lithium chloride on the solubility $S^c(\mathrm{L})_w$, of DB-18-cr-6 in W(DCM) using eq 4.

$$S(\mathrm{L})_w = S^c(\mathrm{L})_w y(\mathrm{L})_w \qquad (4)$$

Furthermore, the ratio $y(\mathrm{L})_o/y(\mathrm{L})_w$ has been derived in the study from the effect of lithium chloride on the partitioning of DB-18-cr-6 (eq 5).

$$P(\mathrm{L}) = P^c(\mathrm{L})y(\mathrm{L})_o/y(\mathrm{L})_w \qquad (5)$$

Combining eqs 4 and 5 yields eq 6

$$P^c(\mathrm{L})S^c(\mathrm{L})_w = P(\mathrm{L})S(\mathrm{L})_w/y(\mathrm{L})_o \qquad (6)$$

Next, the effect of lithium chloride on the extraction

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Table 1. Solubility, *S*, of Crown Ethers or Their Potassium Picrate Complexes in Water (W), Water-Saturated Dichloromethane (DCM(W)) or Dichloromethane (DCM)

ligand or complex	solvent	*T*/K	LiCl added/mol dm^{-3}	*S*/mol dm^{-3}
DB-18-cr-6	W	298.1	0	$(1.65 \pm 0.06) \times 10^{-5}$
DB-18-cr-6	W(DCM)	278.1	0	$(1.03 \pm 0.02) \times 10^{-5}$
		288.1	0	$(1.33 \pm 0.06) \times 10^{-5}$
		298.1	0	$(1.63 \pm 0.04) \times 10^{-5}$
		298.1	0.10	$(1.53 \pm 0.04) \times 10^{-5}$
		298.1	0.25	$(1.38 \pm 0.04) \times 10^{-5}$
18-cr-6·KPi	DCM	297−298	0	0.329
DB-18-cr-6·KPi	DCM	297−298	0	0.171

Table 2. Partition Coefficient, P^c(L), of Crown Ethers between Water and Dichloromethane at 298.1 K (Effect of Lithium Chloride)

L	*C*(LiCl)/mol cm^{-3}	P^c(L)
15-cr-5	0	6.48 ± 0.075^a
	0	3.28^b
18-cr-6	0	3.46^b
	0	4.51 ± 0.29^c
DB-18-cr-6	0	$(2.65 \pm 0.21) \times 10^{4\,a}$
	0.10	$(2.70 \pm 0.24) \times 10^{4\,a}$
	0.25	$(3.02 \pm 0.16) \times 10^{4\,a}$

[a] This study. [b] Inoue *et al.* (1990). [c] Kolthoff (1981).

constant, K^c_{ext}, of DB-18-cr-6·KPi was investigated. When one assumes that $y(L)_o = y(LMPi)_o$ in eq 3, the activity coefficient product, $y(M^+)_w y(Pi^-)_w$, in W(DCM) has been estimated at several concentrations of lithium chloride.

Experimental Section

Dichloromethane (DCM) was Fisher Spectroanalyzed product or MCB Reagent Grade. Viscosities are as follows: DCM 4.11×10^{-4} and DCM(W) 4.17×10^{-4} Pa s (Beronius and Brändström, 1976), 1,2-dichloroethane (DCE) 7.85×10^{-4} (Tucker and Kraus, 1947) and DCE(W) 7.58×10^{-4} Pa s (this work). 18-Crown-6 (Parish, 97% pure) was used previously (Kolthoff and Chantooni, 1980), while dibenzo-18-crown-6 (Parish) was recrystallized from toluene and dried at 363 K. 21-Crown-7 (Parish) was 78.9 mol % pure as estimated from exhaustive extraction as LKPi. It contained ~0.01 mol % K and no detectable Na from flame emission assay. Dibenzo-21-crown-7 (Parish) and lithium hydroxide (Ventron) were used as received. Lithium chloride (Ventron) was recrystallized from 1:1 acetonitrile:water and dried at 380 K. Lithium, sodium, and potassium picrates were prepared as described previously (Kolthoff, 1981). Upon drying at 388 K in vacuo, the first two were found to be monohydrates from spectrophotometric picrate assay in water at 354 nm (molar absorption coefficient, 1.46×10^4 dm^3 mol^{-1} cm^{-1}).

The complexed salt, DB-18-cr-6·KPi, mp 428−429 K, was prepared by evaporating to crystallization a solution in acetone of DB-18-cr-6 and potassium picrate (both 0.05 mol dm^{-3}). For determination of the solubility of 18-cr-6·KPi and of DB-18-cr-6·KPi in DCM, solutions of the crown ether (0.01 to 0.55 mol dm^{-3}) were stirred for 3 days with an excess of finely ground potassium picrate and then filtered. Picrate was determined spectrophotometrically at 370 nm in the filtrate (*v.i.*). Plots of picrate *vs* concentration of crown ether taken passed through the origin and were linear up to the solubility limit (Table 1), beyond which the absorbance remained essentially constant. Stoichiometries correspond to 18-cr-6·1.06KPi and DB-18-cr-6·1.11KPi.

The solubility of dibenzo-18-crown-6 in W(DCM) in the absence or in the presence of lithium chloride was determined by stirring for 1−3 h an excess of the crown ether with a few drops of suspended dichloromethane. After standing for 2 h, a portion was pipeted (outside wiped clean) and then centrifuged. The filtrate was shaken with DCM to back-extract the crown ether, which was determined spectrophotometrically at 275 nm (molar absorption coefficient, 5.88×10^3 dm^3 mol^{-1} cm^{-1}). Four to six replicate runs were performed for each solubility determination.

Partitioning of 15-crown-5 and dibenzo-18-crown-6 between water and DCM was previously described (Frensdorff, 1971). Sodium and potassium picrates, respectively, were used for back-extraction from the aqueous phase. In the extraction of complexed alkali metal picrates DCM(W) solutions of the crown ether (2×10^{-4} to 4×10^{-2} mol dm^{-3}) were shaken with aqueous solutions of alkali metal picrate (1.5×10^{-5} to 2×10^{-2} mol dm^{-3}) and lithium hydroxide (5×10^{-5} mol dm^{-3}). Five to twelve different concentrations of crown ether and picrate were taken in each system. Picrate in DCM(W) was determined spectrophotometrically at 370 nm (molar absorption coefficient: 18-cr-6·NaPi 1.81×10^4, DB-18-cr-6·NaPi 1.71×10^4, 21-cr-7·NaPi 1.58×10^4, 18-cr-6·KPi 1.67×10^4, DB-18-cr-6·KPi 1.67×10^4, and 21-cr-7·KPi 1.72×10^4 dm^3 mol^{-1} cm^{-1}; standard deviation 8×10 dm^3 mol^{-1} cm^{-1}). That of 18-cr-6·LiPi was at the maximum absorption (Table 5). Absorption spectra were recorded on a Cary Model 15 spectrophotometer using 1 or 10 mm stopped quartz cells.

Background electrolytic conductivities, κ, in dichloromethane of 18-crown-6 (0.0139 mol dm^{-3}, $\kappa = 1.3_7 \times 10^{-7}$ S cm^{-1}) or of dibenzo-18-crown-6 (0.0207 mol dm^{-3}, $\kappa = 2.8_7 \times 10^{-7}$ S cm^{-1}) were subtracted from conductivities in potassium picrate solutions containing the same concentration of crown ether. Potassium picrate concentrations were 5.1×10^{-5} to 1.25×10^{-2} and 6.6×10^{-4} to 1.38×10^{-2} mol dm^{-3}, respectively. Conductivity cells and the bridge were those used previously (Kolthoff, and Chantooni, 1962).

Results

Solubility and Partition Constants of Ligands. The solubility of dibenzo-18-crown-6 in pure water at 298.1 K, 1.65×10^{-5} mol dm^{-3}, in Table 1 compares with 2.0×10^{-5} mol dm^{-3} (Kolthoff and Chantooni, 1980), 1.28×10^{-5} mol dm^{-3} (Shchori *et al.*, 1975), and 5.0×10^{-3} mol dm^{-3} in CCl_4 (Shchori *et al.*, 1975). The solubility in W(DCM) at the three temperatures in Table 1 yields $\Delta H = -16.41$ kJ mol^{-1} and $\Delta S = -36.02$ kJ mol^{-1} K^{-1}. If thermodynamic quantities of sublimation of DB-18-cr-6 were available, those of hydration could be obtained. The effect of dissolved DCM in water on the solubility is small. Concentration partition coefficients, P^c(L), of 15-crown-5 and dibenzo-18-crown-6 between DCM(W) and W(DCM) at 298.1 K are entered in Table 2. The present value of *P*(DB-18-cr-6) in DCM(W) at zero ionic strength, 2.65×10^4, compares with 8.0×10^3 in $CHCl_3$ (Hasegawa *et al.*, 1981) and 1.0×10^4 in CH_2ClCH_2Cl (Kina *et al.*, 1978), in the order expected from the π^* dipolarity index of chlorohydrocarbons (Kamlet *et al.*, 1983).

Extraction of Complexed Alkali Picrates from Water into DCM. Values of the logarithm of the extraction

Table 3. Extraction Parameters of Alkali Metal Picrates Complexed with Unsubstituted or Dibenzo-Substituted Crown Ethers between Water and Dichloromethane at 298.1 K

electrolyte	K_A(LMPi) × 10^{-4}/ mol^{-1} dm^3	log K_{ex}
18-cr-6·LiPi	1.7^e	2.163 ± 0.031^e
		$7.43^{f,i}$
18-cr-6·NaPi	1.1^b	3.34^b
	3.3^c	3.08^c
		3.89^f
DB-18-cr-6·NaPi	11.1^e	2.631 ± 0.029^e
		2.81^f
DB-21-cr-7·NaPi	$(11)^h$	$(2.3)^e$
18-cr-6·KPi	3.3^b	6.21^b
	10^c	5.48^c
		6.20^f
	7.44^d	6.04^g
	5.0^e	6.386 ± 0.021^e
DB-18-6·KPi	22.7^a	5.85^a
	50.6^d	4.84^f
	33.3^e	4.887 ± 0.008^e
		5.23^g
DCC-18-cr-6·KPi (A)	4.0^a	6.6^a
DB-21-cr-7·KPi	$(33)^h$	$(4.5)^e$

[a] Frensdorff (1971). [b] Kolthoff (1981). [c] Kopolow, S.; Hogen-Esch, T. E.; Smid, J. *Macromolecules* **1973**, *6*, 133. [d] This work (K_A from conductance data). [e] This work (K_A from extraction data). [f] Inoue *et al.* (1990). [g] Buncel, E.; Shin, H. S.; Bannard, R. A. B.; Purdon, J. G. *Can. J. Chem.* **1984**, *62*, 926. [h] K_A(DB-21-cr-7·MPi) assumed same as K_A(DB-18-cr-6·MPi). [i] L(MPi)$_2$ reported to be extracted.

constant, log K_{ex}, and corresponding association constant of the complexed picrate salts, K_A(LMPi), are assembled in Table 3. Since extractions involving dibenzo-21-crown-7 were carried out at only one concentration of crown ether and picrate, values of K_{ex} in Table 3 are in parentheses. Values of log K_A(LKPi) from extraction agree to within 0.18 unit with those from conductance. When dissociation of LMPi in the organic phase is neglected, the calculated value of K_{ex} becomes too large, particularly when dilute solutions are partitioned and K_A(LMPi) is small. Calculation of the crown ether concentration in both phases using the partition coefficient, P^c(L), has been described by Inoue *et al.* (1988). The following relations, regarding MPi to be completely dissociated in water, were used:

$$(C_L)\ \text{total} = [L]_w + [LM^+]_w + [L]_o + [LM^+]_o + [LMPi]_o \tag{7}$$

$$(C_{MPi})\ \text{total} = [M^+]_w + [LM^+]_w + [LM^+]_o + [LMPi]_o \tag{8}$$

First, various values of K_A(LMPi) were assumed and the one taken was that which yields the minimum in the quantity (standard deviation of K_{ex}/K_{ex}) (Frensdorff, 1971). Activity coefficients, $y(M^+)$ and $y(Pi^-)$, in the aqueous phase were evaluated using the partially extended Debye−Hückel expression $-\log y = 0.5115 I^{1/2}/(1 + 3.29 a I^{1/2})$, taking a = 0.60, 0.40, 0.30, and 0.70 nm for Li^+, Na^+, K^+, and Pi^-, respectively. Using the above value of K_A(LMPi) the data were recalculated, considering in addition, ionic activity coefficients in DCM(W) according to the expression $-\log y = 13.202/I^{1/2}/(1 + 3.89 I^{1/2})$. The symbol I denotes ionic strength. At most, only ~0.3% of LKPi in the organic phase is in the form of triple ions (*vi*).

In extractions involving high concentrations of lithium chloride, the above procedure was followed, assuming K_A(LMPi) to be the same as in its absence. Under our experimental conditions coextracted DB-18-cr-6·LiPi is ≤1% that of DB-18-cr-6·KPi and was neglected.

Table 4. Conductance Parameters of Crown Complexes of Potassium Picrate in Water-Saturated Dichloromethane at 298 K

parameter	18-cr-6·KPi	DB-18-cr-6·KPi
Λ_o(LKPi)/S cm^2 mol^{-1}	99.8^a $(87.1)^b$	113.8^a
$\lambda_o(LK^+)^c$/S cm^2 mol^{-1}	31.8^a	45.8^a
K_A(LKPi)/mol^{-1} dm^3	7.44×10^4,^{d} $(4.5 \times 10^4)^e$	$5.06 \times 10^{5\ d}$
a_i/nm	0.57	0.43
Λ_{o3}/S cm^2 mol^{-1}	70^f	80^f
K_3/mol^{-1} dm^3	(1.8×10^1)	(9.8)

[a] From $\eta\lambda_o(LK^+)$ product and $\lambda_o(Pi^-)$; see text. [b] From intercept of Fuoss and Kraus plot. [c] For comparison, $\lambda_o(Bu_4N^+) = 38.4$; see text. [d] From intercept of $\Lambda y^{\pm} c^{1/2}/F(z)$ vs c plot and Λ_o(LKPi) referred to by footnote *a*. [e] From slope and intercept of Fuoss and Kraus plot. [f] Assumed value.

Conductance of LKPi Solutions in DCM(W). Owing to the poor dissociation of LKPi in DCM(W), an accurate value of the sum of ionic mobilities at infinite dilution, Λ_o(LKPi), could not be obtained from a Fuoss and Kraus plot. A rough estimate of Λ_o(18-cr-6-KPi) in Table 4 (footnote *b*) was made from the linear portion ($c = 5 \times 10^{-5}$ to 5×10^{-3} mol dm^{-3}). Alternatively, Λ_o values were found by assuming $\eta\lambda_o$ independent of solvent. First, $\lambda_o(Pi^-)$ in DCM(W) was estimated as follows: Taking $\Lambda_o(Ph_4AsBPh_4) = 88.1$ and $\Lambda_o(Bu_4NBPh_4) = 83$ S cm^2 mol^{-1} in dry DCM (Svorstøl and Songstad, 1985) and assuming $\lambda_o(Ph_4As^+) = \lambda_o(BPh_4^-)$, $\lambda_o(Bu_4N^+) = 38.95$ S cm^2 mol^{-1} (Ph = C_6H_5, Bu = n-C_4H_9). From the Walden product, $\lambda_o(Bu_4N^+)$ equals 38.38 S cm^2 mol^{-1} in DCM(W). The solvents CH_3CHCl_2 and CH_2ClCH_2Cl (DCE) are sufficiently similar in polarity to DCM(W) that the products $\eta\Lambda_o(Bu_4NPi)$, 0.4496 (Healey and Martell, 1951) and 0.4353 (Mead *et al.*, 1936) S cm^2 mol^{-1} Pa s, respectively, were averaged. Hence, $\Lambda_o(Bu_4NPi) = 106.4$ S cm^2 mol^{-1} in DCM(W), which is in line with those of $(n\text{-}Pr)_4NPi$, 110.7, and Et_4NPi, 125.4 S cm^2 mol^{-1} (Beronius and Brändström, 1976). Therefore, $\lambda_o(Pi^-)$ in DCM(W) = 106.4 − 38.4 = 68.0 S cm^2 mol^{-1}, as compared to 66 reported by Beronius and Brändström (1976). For estimation of Λ_o(18-cr-6·KPi) in DCM(W) in Table 4 $\lambda_o(18\text{-cr-}6\cdot K^+)$ in DCE(W) is first evaluated from Λ_o(18-cr-6·KPi) = 48.64 (Kolthoff *et al.*, 1993) and $\lambda_o(Pi^-) = 31.20$ S cm^2 mol^{-1} (Chantooni and Kolthoff, 1992). Assuming a constant $\eta\lambda_o^+$ product, $\lambda_o(18\text{-cr-}6\cdot K^+)$ in DCM(W) = 31.79 (Table 4). The value of Λ_o(DB-18-cr-6·KPi) in DCM(W) in Table 4 was estimated simarily, taking $\Lambda_o(\text{DB-18-cr-6}\cdot KPiCl_2) = 48.22$ (Kolthoff *et al.*, 1993) and $\lambda_o(PiCl_2^-) = 23.00$ S cm^2 mol^{-1} (Chantooni and Kolthoff, 1992) in DCE(W) ($PiCl_2^-$ = dichloropicrate).

Conductance data over the entire concentration range were analyzed for one kind of triple ion (French and Roe, 1953). Plots of $\Lambda[c(K_3' + c)]^{1/2}$ *vs* c were linear over a wide range of K_3' rather than at a unique value. Conductance data, therefore, were treated according to bilateral triple ion formation (Fuoss and Kraus, 1933a,b).

$$3LKPi \rightleftharpoons (LK)_2Pi^+ + LKPi_2^-$$

$$K_3 = [(LK)_2Pi^+]/[LKPi][LK^+] = [LKPi_2^-]/[LKPi][Pi^-] \tag{9}$$

Plots of $\Lambda y^{\pm} c^{1/2}/F(z)$ *vs* c were linear over the entire concentration range. The constants K_A(LKPi) (equal to Λ_o^2(LKPi)/(intercept)^2) and K_3 (equal to slope $K_A^{1/2}(LKPi)/\Lambda_{o3}$) were estimated, where Λ_{o3} denotes the sum of the molar conductivities of both triple ions. The intercept and slope of the above plots are 0.366, 4.47 for 18-cr-6·KPi and 0.159, 1.19 for DB-18-cr-6·KPi. Values of Λ_{o3} and K_3 are in Table 4.

Table 5. Molar Absorption Coefficient (ϵ) at Absorption Maximum (λ_m) of Complexed Alkali Model Picrates in Dichloromethane Saturated with Water

	Na		K	
ligand	λ_m/nm	$\epsilon \times 10^4$/dm^3 mol^{-1} cm^{-1}	λ_m/nm	$\epsilon \times 10^4$/dm^3 mol^{-1} cm^{-1}
15-cr-5	360[a]	1.69[a]	375[a]	1.70[a]
	358[c]		367[c]	
18-cr-6[d]	367[a]	1.83[a]	369[a]	1.67[a]
			369[b]	1.79[b]
			375[c]	
DB-18-cr-6	365[a]	1.73[a]	364[a]	1.74[a]
21-cr-7	363[a]	1.63[a]	373[a]	1.73[a]

[a] This study. [b] Kolthoff (1981). [c] Inoue *et al.* (1987). [d] For 18-cr-6·LiPi $\epsilon = 1.48 \times 10^4$ dm^3 mol^{-1} cm^{-1} at λ_m 352 nm.

Discussion

Nature of Crown Ether Complexes with Potassium Picrate Ion Pairs. Due to the electron-withdrawing effect of the phenyl groups in DB-18-cr-6, the basicity of its crown ether oxygens is less than in dicyclohexano-18-crown-6 isomer A (DCC-18-cr-6) or in 18-cr-6 (Kolthoff *et al.*, 1983). Consequently, the effective charge on K^+ in DB-18-cr-6·K^+ is screened to a lesser extent than in 18-cr-6·K^+. In solvents of low donicity, e.g. CH_2Cl_2, K^+ in DB-18-cr-6·K^+-Pi^- can then approach close to Pi^-. This results in K_A(DB-18-cr-6·KPi) being almost 1 order of magnitude larger than that of 18-cr-6·KPi or DCC-18-cr-6·KPi (Table 3) and is true for the analogous sodium picrate complexes. Conformational effects, such as ligand rigidity, also are significant (Takeda, 1983). The corresponding value of the Bjerrum distance of closest approach of ion centers, a_i, in DB-18-cr-6·KPi, 0.43 nm, (Table 4) is considerably less than that in 18-cr-6·KPi, 0.57 nm. The latter is in the range of 0.55 to 0.65 nm found for Bu_4NPi in several dipolar aprotic solvents (Kolthoff and Chantooni, 1979). The charge on Bu_4N^+ is well shielded from the solvent and from Pi^- (Takeda, 1983). Taking $a_i = 0.57$ nm as an average for Bu_4NPi and the solvatodynamic radius of Bu_4N^+, 0.35 nm (Arrington and Griswold, 1970), $a_i(Pi^-) = 0.57 - 0.35 = 0.22$ nm.

Additional information regarding the charge on Pi^- in the crown-complexed alkali picrates can be ascertained from the location of the maximum in the electronic absorption spectrum, λ_m, of undissociated LMPi in CH_2Cl_2 (Inoue *et al.*, 1987). The maximum of "free" picrate in cryptand 2.2.2 KPi occurs at 375 nm (Inoue *et al.*, 1987). From the order of λ_m in Table 5, 21-cr-7·KPi > 18-cr-6·KPi > DB-18-cr-6·KPi > 15-cr-5·NaPi ≫ 18-cr-6·LiPi (λ_m 352 nm, $\epsilon = 1.48 \times 10^4$ mol^{-1} cm^{-1} (this work)), it is surmised that Pi^- in 18-cr-6·KPi behaves more like a "free" picrate than does Pi^- in DB-18-cr-6·KPi. Only a rough inverse correlation between λ_m(LMPi) and K_A(LMPi) can be expected. The occurrence of λ_m at 375 nm in a solution 4×10^{-3} mol dm^{-3} in 15-cr-5 and 6.7×10^{-5} mol dm^{-3} in KPi (Table 5) likely is attributed to the sandwich complex $(15\text{-cr-}5)_2$·KPi in which K^+ is well shielded.

In solvents of higher dielectric permittivity, the solvent can solvate the encased K^+ axially in DB-18-cr-6·KPi, while Pi^- comes close on the other side (Takeda, 1983). When one compares the solvation of LK^+ in propylene carbonate (PC) and dimethyl sulfoxide (DMSO), solvents of widely differing ionicity, the free energy of transfer, $\Delta G_{tr}°[(18\text{-cr-}6·K^+)PC \rightarrow DMSO]$ is -2.1 kJ mol^{-1}, as compared to $\Delta G_{tr}[(DB\text{-}18\text{-cr-}6·K^+)PC \rightarrow DMSO] = -8.8$ kJ mol^{-1} (Chantooni *et al.*, 1988).

Table 6. Concentration Extraction Constant, K^c_{ex}, of DB-18-cr-6·KPi in the Presence of Lithium Chloride in the Aqueous Phase (Activity Coefficients of Various Species)

		activity coeff		
C(LiCl)/mol dm^{-3}	$K^c \times 10^{-4}$ [a]/ (mol^{-2} dm^6)	$y(L)_w$	$y(L)_o$	$y(K^+)_w y(Pi^-)_w / y(LKPi)_o$
0.05	5.61		~1.03[b]	~0.69
0.10	4.94	1.06_5	1.04_0	0.59_9
0.25	4.60	1.18_1	1.04_3	0.56_0

[a] K_{ex} at zero ionic strength = $7.8_8 \times 10^4$. [b] Interpolated value.

Mobility of Complexed Potassium Ion. Values of $\lambda_o(LK^+)$ in acetonitrile, *N,N*-dimethylformamide, PC, and DMSO are in the order $\lambda_o(Bu_4N^+) > \lambda_o(18\text{-cr-}6·K^+) > \lambda_o(DB\text{-}18\text{-cr-}6·K^+)$ (Takeda, 1983), while in DCM(W) the order is $\lambda_o(DB\text{-}18\text{-cr-}6·K^+) > \lambda_o(Bu_4N^+) > \lambda_o(18\text{-cr-}6·K^+)$ (Table 4). Lack of strong solvation of DB-18-cr-6·K^+ in DCM(W) very likely is responsible for its high mobility.

Triple Ion Formation. Although the purely electrostatic Bjerrum treatment (Fuoss and Kraus, 1933a) regards the two types of triple ions $(LM)_2Pi^+$ and $LMPi_2^-$ as symmetrical (similar in size and ionic mobility), in reality, they are likely to be asymmetric. Close approach of Pi^- to K^+ in the DB-18-cr-6·K^+Pi^- ion pair would result in a smaller dipole moment than in 18-cr-6·K^+Pi^-. Hence, the second Pi^- (or DB-18-cr-6·K^+) in the triple ion lies further away from the opposite charge on the K^+-Pi^- dipole and K_3 is smaller (Table 4).

Activity Coefficients in Concentrated Aqueous Lithium Chloride Solutions. From the solubility of DB-18-cr-6 in the presence of lithium chloride in Table 1, $y(L)_w$ was calculated from eq 4 and entered in Table 6. The activity coefficient $y(L)_o$ in Table 6 was derived from $P^c(L)$ at the same concentration of lithium chloride using eq 6. Complexation of Li^+ by DB-18-cr-6 is negligible. The Setchenow "salting out" coefficient, $k = 0.28_1$, in the relation $\log y(L)_o = kc(LiCl)$ (Lewis and Randall, 1961) is reasonable for a simple diaryl nonelectrolyte. It is evident from Table 6 that the effect of ionic strength on partitioning equilibria of DB-18-6·KPi is due mainly to the activity coefficients of the uncomplexed ions in water; that of salting out of L is almost negligible.

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