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Partitioning of Crown Ether Complexed Univalent Metal Dichloropicrates between Water and 1,2-Dichloroethane at 298 K. Thermodynamic Representation

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The extraction constant of silver and cesium dichloropicrate ($MPiCl_2$) between water and 1,2-dichloroethane in the presence of 18-crown-6 or dibenzo-18-crown-6 (L) has been expressed in terms of the Gibbs free energy of transfer of M^+ and $PiCl_2^-$, the association constant of $LMPiCl_2$ ($K_A(LMPiCl_2)$), and the stability constant of LM^+ ($K_f(LM^+)$) in the organic phase. This has been verified experimentally by partitioning $MPiCl_2$ alone. Using suitable extrathermodynamic assumptions, $\Delta G^\circ_{tr}(PiCl_2^-) = 3.8$ kJ mol^{-1}, as compared to $\Delta G^\circ_{tr}(Pi^-) = -7.0$ kJ mol^{-1}. This imparts favorable extractability to $LMPiCl_2$. In addition, sodium, potassium, and thallium dichloropicrate extraction equilibria involving the above crown ethers are reported.

Introduction

About 20 years ago, it was found that uncomplexed alkali-metal salts, MX, having large lipophilic anions, i.e., picrate (Pi^-) (*1*), (2,4,6,2′,4′,6′-hexanitrodiphenyl)aminate (*2*), tetraphenylborate (BPh_4^-) (*3*), and even perchlorate (*3*) can be readily extracted from water (W) into nitrobenzene. Ion pairing occurs to a varying extent in both phases. When a neutral complexing ligand, L, is added to the "immiscible" organic solvent, M^+ is transformed into a lipophilic cation, LM^+, thereby greatly enhancing the extractability of the above salts (*4*). Kyrš et al. (*5*) related the extraction constant, K_{ex}, to the Gibbs free energy of transfer of M^+ and X^- from the organic solvent saturated with water, O(W), to water saturated with the organic solvent, W(O), by eq 1. The symbol $y^\pm$

$$\log K_{ex}' = \log\{[LM^+]_{O(W)}[X^-]_{O(W)}(y^\pm)^2\} - \log\{[L]_{O(W)}[M^+]_{W(O)}[X^-]_{W(O)}\} = \log K_f(LM^+) + \Delta G^\circ_{tr}(M^+ + X^-)_{O(W)\to W(O)}/RT \ln 10 \quad (1)$$

$$K_f(LM^+) = [LM^+]_{O(W)}/[L]_{O(W)}[M^+]_{O(W)} \qquad y(LM^+) = y(M^+) \quad (2)$$

denotes the Debye–Hückel mean ionic activity coefficient in O(W), that in water being close to unity. Ion pairing has been neglected in both solvents. In organic solvents of low dielectric permittivity the extracted species is primarily the ion pair LMX, designated here as uncharged. Extraction equilibria of MX in the absence and presence of L, as represented by Scheme I for the immiscible solvents W and O, has been discussed in an excellent review article (*6*).

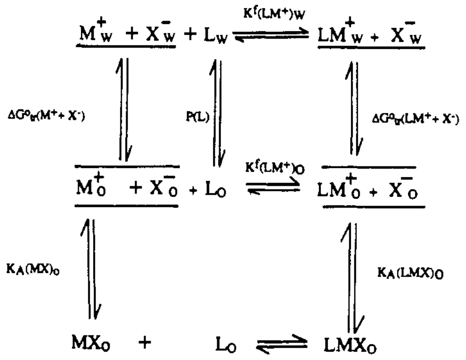
The quantities D, K_{ex}, and P(L) are defined customarily as

$$D = [MX]_{O(W)}/[M^+]_{W(O)}[X^-]_{W(O)} \quad (3)$$

$$K_{ex} = [LMX]_{O(W)}/[L]_{O(W)}[M^+]_{W(O)}[X^-]_{W(O)} \quad (4)$$

$$P(L) = [L]_{O(W)}/[L]_{W(O)} \quad (5)$$

Scheme I



In this case the extraction constants D and K_{ex} can be expressed in terms of $\Delta G^\circ_{tr}(M^+ + X^-)_{O(W)\to W(O)}$ by eqs 6 and 7. Yoshio and Noguchi (*6*) observed that K_{ex}/D between

$$\log K_{ex} = \log K_A(LMX)_{O(W)} + \Delta G^\circ_{tr}(M^+ + X^-)_{O(W)\to W(O)}/RT \ln 10 + \log K^f(LM^+)_{O(W)} \quad (6)$$

$$\log(K_{ex}/D) = \log K_A(LMX)_{O(W)} - \log K_A(MX)_{O(W)} + \log K^f(LM^+)_{O(W)} \quad (7)$$

nitrobenzene and water for DB-18-cr-6MPi (dibenzo-18-crown-6 = DB-18-cr-6) correlates linearly with K_f(DB-18-cr-6M^+) in propylene carbonate (PC).

In this study, 1,2-dichloroethane (DCE) was chosen because its polarity allows good extractability of the uncomplexed dichloropicrates. Values of K_{ex} between water and DCE of $MPiCl_2$ complexed with 18-crown-6 (18-cr-6) or with DB-18-cr-6 were estimated, M being Na, K, Cs, Tl, or Ag and $PiCl_2^-$ = dichloropicrate. The constants $K_A(MPiCl_2)$ and $K_A(LMPiCl_2)$ in DCE and in DCE(W) were determined conductometrically, and $K^f(LAg^+)$ was determined potentiometrically in DCE(W) with the Ag electrode. To establish the internal consistency of Scheme I, resulting values of $\Delta G^\circ_{tr}(Ag^+ + PiCl_2^-)_{DCE(W)\to W(DCE)}$ and $\Delta G^\circ_{tr}(Cs^+ + PiCl_2^-)_{DCE(W)\to W(DCE)}$ calculated from eq 6 were compared with those derived from partitioning uncomplexed $AgPiCl_2$ and independently from the solubility products of $AgPiCl_2$ in W(DCE)

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Table I. Association Constants and Solubility Products ($\Delta G^\circ_s = -RT \ln K^{sp}$) of Uncomplexed Silver and Cesium Salts on the Molar Scale at 298 K

salt	solvent	Λ_0/ (S cm^2 mol^{-1})	K_A/ (mol^{-1} dm^3)	conduct. of satd soln/ (S cm^{-1})	solubility/ (mol dm^{-3})	y^+y^-	ΔG°_s/ (kJ mol^{-1})
$AgClO_4$	DCE	75.9[a]	1.6×10^6 [d]	6.86×10^{-6}	6.94×10^{-3}		
$AgClO_4$	DCE(W)	80.9[a]	9.1×10^6				
$AgPiCl_2$	DCE	52.7[a]	1.7×10^7 [d]	5.58×10^{-7}	1.30×10^{-3}	0.848	57.3
$AgPiCl_2$	DCE(W)	60.8[a]	7.2×10^6	1.19×10^{-6}	2.28×10^{-3}	0.809	54.1
$AgPiCl_2$	PC	23.81	7.8×10^1	7.25×10^{-4}	0.127	0.780	16.9
$AgPiCl_2$	W	91.52	<5	4.27×10^{-3}	0.0605	0.655	15.0
$AgPiCl_2$	W(DCE)	91.52[b]	<5	4.85×10^{-3}	0.0676	0.639	14.3
$CsPiCl_2$	DCE	54.2[c]		9.06×10^{-7}		0.813	54.8
$CsPiCl_2$	DCE(W)	62.4[c]	2.4×10^6	7.02×10^{-7}	2.60×10^{-4}	0.847	56.8
$CsPiCl_2$ $2H_2O$	W	106.9	<5	1.15×10^{-3}	0.0125	0.903	22.5
$CsPiCl_2$ $2H_2O$	W(DCE)	106.9[b]	<5	1.15×10^{-3}	0.0126	0.902	22.3

[a] From $\lambda_0(Ag+) = 36.0$ S cm^2 mol^{-1} in DCE and 37.7 S cm^2 mol^{-1} in DCE(W) [estimated from the product $\eta\lambda_0(Ag^+) = 0.0286$ S cm^2 mol^{-1} Pa s in PC (Courtot-Coupez, J.; L'Her, M. *C.R. Acad. Sci., Ser. C* **1970**, 357)] and $\eta\lambda_0(ClO_4^-)$ or $\eta\lambda_0(PiCl_2^-)$. [b] $\Lambda_0(MPiCl_2)$ in W(DCE) assumed the same as in W. [c] From $\lambda_0(Cs^+) = 37.5$ S cm^2 mol^{-1} in DCE and 39.3 S cm^2 mol^{-1} in DCE(W), estimated from $\eta\lambda_0(Cs^+) = 0.0298$ S cm^2 mol^{-1} Pa s in acetonitrile [Springer, C. H.; Coetzee, J. F.; Kay, R. L. *J. Phys. Chem.* **1969**, *73*, 471] and $\lambda_0(PiCl_2^-)$. [d] Triple ion also present, $K^t \approx 1 \times 10^2$ mol^{-1} dm^3.

and in DCE(W). The latter two experiments were performed with $CsPiCl_2$. Free energies of transfer of single ions in this study were derived from those of $\Delta G^\circ_{tr}(Ag^+)_{DCE\rightarrow DCE(W),PC}$ and $\Delta G^\circ_{tr}(Ag^+)_{PC\rightarrow W}$. The first is based on the Lejaille and Bessière extrathermodynamic assumption (*7*):

$$\Delta G^\circ_{tr}(C222Ag^+)_{R\rightarrow S} = \Delta G^\circ_{tr}(C222)_{R\rightarrow S} \qquad (8)$$

or

$$\log K_f(C222Ag^+)_S - \log K^f(C222Ag^+)_R = \Delta G^\circ_{tr}(Ag^+)_{R\rightarrow S} \qquad (9)$$

where C222 = cryptand 2.2.2, R = DCE as reference solvent, and S = DCE(W) or PC. The second is based on Parker's TATB assumption (*8*):

$$\Delta G^\circ_{tr}(Ph_4As^+)_{R\rightarrow S} = \Delta G^\circ_{tr}(BPh_4^-)_{R\rightarrow S} \qquad (10)$$

Experimental Section

1,2-Dichloroethane was an Aldrich Gold Label product (**note:** *environmentally hazardous*). Dibenzo-18-crown-6 (*9*), 18-crown-6 (*9*), and cryptand 2.2.2 (*10*) were products used previously. Electrolytic conductivities of 1,2-dichloroethane and 1,2-dichloroethane saturated with water were $<1 \times 10^{-9}$ and 5.0×10^{-9} S cm^{-1}, respectively. Background electrolytic conductivities of the ligands (0.011 mol dm^{-3}) in DCE(W) did not exceed 4×10^{-7} S cm^{-1}, with the exception of 18-crown-6, which was 1.8×10^{-6} S cm^{-1}. These conductivities were deducted from those obtained with electrolytes. Silver, sodium, potassium, cesium, and thallium dichloropicrates were prepared by neutralizing the oxide or hydroxide with dichloropicric acid in water, filtering if necessary, and crystallizing the salts upon cooling. They were dried at atmospheric pressure for 3 h at 350 K. The purity by spectrophotometric dichloropicrate assay in water (molar absorption coefficient at 380 nm, 4.18×10^3) was 99.0–100.5%. Silver perchlorate was that used previously (*9*). Extractions were performed by shaking both phases for 10–12 h, separating the layers, and centrifuging. 18-Crown-6 was determined spectrophotometrically at 398 nm following exhaustive extraction with potassium dichloropicrate (0.01 mol dm^{-3}) instead of picrate (*11*) into dichloromethane. The molar absorption coefficient of 18-cr-6KPiCl$_2$ varied from 5.40×10^3 to 5.00×10^3, concentrations being 0–1.5×10^{-4} mol dm^{-3}. The total dichloropicrate content of the DCE(W) phase was determined spectrophotometrically upon taking an aliquot to dryness and making up to a given volume with water. Total solubilities of dichloropicrates were found in the same way as for picrates (*12*).

Table II. Extraction Parameters of Complexed Univalent Dichloropicrate Salts between Water and 1,2-Dichloroethane at 298 K

electrolyte	Λ_0[a]/ (S mol^{-1} cm^2)	$K_A \times 10^{-3}$ [a]/ (mol^{-1} dm^3)	log (K_{ex})	$K_f(LM^+)$/ (mol^{-1} dm^3)
18-cr-6NaPiCl$_2$	46.9_4	7.7	7.0_0	
DB-18-cr-6NaPiCl$_2$	54.4_8	$46._5$	4.8_6	
18-cr-6KPi	48.6_4	9.6_8	6.5_7	
18-cr-6KPiCl$_2$	45.6_6	3.3_7	8.0_1	
DB-18-cr-6KPiCl$_2$	48.2_2	34[b]	6.6_4	
18-cr-6CsPiCl$_2$	50.1_8	2.0_0	6.8_3	1.6×10^{10} [a,c]
18-cr-6TlPiCl$_2$	51.4_4	2.0_7	8.6_3	
DB-18-cr-6TlPiCl$_2$	45.8_4	4.7_5	6.7_8	
18-cr-6AgPiCl$_2$	47.7	1.3_8	7.0_4	$(5.03 \pm 0.68) \times 10^{10}$ [a]
DB-18-cr-6AgPiCl$_2$	40.1_5	4.0_9	5.4_5	$(5.28 \pm 2.11) \times 10^8$ [a]
C222Ag PiCl$_2$	49.9	0.40		$(1.85 \pm 0.36) \times 10^{20}$ [a]
C222Ag PiCl$_2$	44.3_2[d]	<0.02[d]		$(3.03 \pm 0.38) \times 10^{20}$ [d]

[a] Solvent DCE(W). [b] In addition, K^t(triple ion) $\approx 7 \times 10^1$ mol^{-1} dm^3. [c] Calculated from eq 7, taking $D = 0.50$ mol^{-1} dm^3 for uncomplexed $CsPiCl_2$. [d] Solvent, water-free DCE.

All spectrophotometric measurements were made on a GCA McPherson EU-700 spectrophotometer. For potentiometric measurements an Orion 701A potentiometer was used in conjunction with the three-compartment cell described previously (*13*). One of the end compartments contained the Ag/AgClO$_4$ (0.0113 mol dm^{-3}) reference half-cell, while the middle compartment was filled with tetrabutylammonium perchlorate (0.005 mol dm^{-3}) in DCE or DCE(W). Silver electrodes were platinum 4-mm wire plated with silver. The potential of this electrode generally stabilized within 20 min, being reproducible to within ±2 mV. No auxiliary electrolyte was used to maintain a high constant ionic strength, as this would introduce additional equilibria.

Results

Association Constants of Salts. Association constants of dichloropicrates are needed for evaluation of the various equilibrium constants. As concluded from conductance data, $AgPiCl_2$ and $CsPiCl_2$ are practically completely dissociated in their saturated solutions in W and in W(DCE) (Table I), as well as C222AgPiCl$_2$ in DCE (Table II). Salt concentrations were 5×10^{-5} to 3×10^{-3} mol dm^{-3}. To ensure complete complexation, an excess of ligand was maintained at 0.011 mol dm^{-3}. Values of Λ_0 and K_A entered in Table II were obtained from conductance data using the Fuoss and Kraus treatment (*14*). Ionic mobilities in DCE and in DCE(W) are

$\lambda_0(\mathrm{PiCl_2^-})$ = 16.7 (*15*) and 23.1 (*15*) S cm^2 mol^{-1}, while $\Lambda_0(\mathrm{Et_4NClO_4})$ = 75.9$_5$ S cm^2 mol^{-1} and $K_A = 7.8 \times 10^5$ dm^3 mol^{-1} in DCE(W). The salts $\mathrm{AgPiCl_2}$, $\mathrm{CsPiCl_2}$, and $\mathrm{AgClO_4}$ are too slightly dissociated in DCE and DCE(W) to yield Λ_0 from the Fuoss and Kraus treatment. Therefore, Λ_0 was approximated, using the product $\eta\lambda_0(\mathrm{M^+})$ in acetonitrile or PC to evaluate $\lambda_0(\mathrm{M^+})$, η being viscosity. The above approximation introduces an uncertainty of ±0.2 kJ mol^{-1} in ΔG°_s in Table I. Viscosities of DCE and DCE(W) at 298 K are 7.95×10^{-4} (*16*) and 7.58×10^{-4} (*15*) Pa s, respectively. Viscosity corrections were not made in the presence of ligands. The presence of a triple ion in DCE solutions of silver dichloropicrate was deduced from curvature in the Fuoss and Kraus plot. The conductance data therefore were analyzed according to the method of French and Roe (*17*), assuming λ_0(triple ion) = 8.0 S cm^2 mol^{-1}.

Solubility Product of Uncomplexed Salts. These are required for calculation of the free energy of transfer of MX. Table I lists the total solubility in the saturated solution and the solubility products of $\mathrm{AgPiCl_2}$ and $\mathrm{CsPiCl_2}$. As the total solubilities of sodium, potassium, and thallium dichloropicrates in DCE(W) were $<1 \times 10^{-5}$ mol dm^{-3}, these salts were not used. In this study, solid $\mathrm{AgPiCl_2}$ was found to be unsolvated in all the solvents taken, as well as $\mathrm{CsPiCl_2}$ in DCE and in DCE(W). The latter salt forms a stable dihydrate in water (*18*) and presumably also in W(DCE).

Complexation Constants of Silver Ion with Ligands in DCE and in DCE(W). Values of $K_f(\mathrm{LAg^+})$ in DCE or in DCE(W) entered in the last column of Table II were estimated from $a(\mathrm{Ag^+})$ obtained from the potential of the silver electrode in solutions of (1–3) $\times 10^{-3}$ mol dm^{-3} in $\mathrm{AgPiCl_2}$ and 4×10^{-3} to 0.05 mol dm^{-3} in 18-cr-6 or C222. In PC log $K_f(\mathrm{C222Ag^+})$ = 16.54 (*10*). Owing to the limited solubility of DB-18-cr-6AgPiCl$_2$ in DCE(W), solutions were only 2.6×10^{-4} to 1×10^{-3} mol dm^{-3} in $\mathrm{AgPiCl_2}$ and 1.9×10^{-3} to 0.03 mol dm^{-3} in DB-18-cr-6.

The total silver concentration, $C(\mathrm{AgPiCl_2})$, in mixtures of L and $\mathrm{AgPiCl_2}$ is

$$C(\mathrm{AgPiCl_2}) = [\mathrm{Ag^+}] + [\mathrm{AgPiCl_2}] + [\mathrm{LAg^+}] + [\mathrm{LAgPiCl_2}] \quad (11)$$

while the total ligand concentration is

$$C(\mathrm{L}) = [\mathrm{L}] + [\mathrm{LAg^+}] + [\mathrm{LAgPiCl_2}] \approx [\mathrm{L}] + C(\mathrm{AgPiCl_2}) \quad (12)$$

Neglecting $[\mathrm{Ag^+}]$ and $[\mathrm{AgPiCl_2}]$ in eq 11, $[\mathrm{LAg^+}]$ has been calculated from $C(\mathrm{AgPiCl_2})$ using $K_A(\mathrm{LAgPiCl_2})$ from Table II, while [L] is found from eq 12. Values of $K_f(\mathrm{LAg^+})$ in DCE(W) are 3–4 orders of magnitude greater than those in PC, the solvent in which the largest values previously have been reported (*9*). An attempt to ascertain $K_f(\text{18-cr-6Cs}^+)$ in DCE(W) by using the disproportionation reaction

$$\text{18-cr-6Ag}^+ + \mathrm{Cs^+} \rightleftharpoons \text{18-cr-6Cs}^+ + \mathrm{Ag^+}$$

was unsuccessful, owing to the excessive complexation of $\mathrm{Cs^+}$ in the mixtures of 18-cr-6, $\mathrm{AgPiCl_2}$, and $\mathrm{CsPiCl_2}$.

Partitioning of Ligands and of Uncomplexed Metal Dichloropicrates. The partition coefficient, $P(\mathrm{L})$, at 298 K (eq 5) was estimated by partitioning 18-cr-6 between equal volumes of DCE(W) and W(DCE). The aqueous phase was (2.5–9.1) $\times 10^{-4}$ mol dm^{-3} in L. The resulting values of $P(\mathrm{L})$ = 0.910 ± 0.086 is in excellent agreement with that derived from extraction data of 18-cr-6MPiCl$_2$, 0.923 ± 0.169 and the value 1.12, reported by Yoshio et al. (*6*). For 18-cr-6, a value of $P(\mathrm{L})_{\mathrm{PC}\to\mathrm{W}} = 0.0481$ was calculated from $P(\mathrm{L})_{\mathrm{hexadecane}\to\mathrm{PC}} = 8.11 \times 10^{-3}$ (*19*) and $P(L)_{\mathrm{hexadecane}\to\mathrm{W}} = 3.9 \times 10^{-4}$ (*20*).

In a separate study, $\mathrm{AgPiCl_2}$, 3.5×10^{-3} to 0.013 mol dm^{-3}, or $\mathrm{CsPiCl_2}$, (3.5–7.1) $\times 10^{-3}$ mol dm^{-3}, was partitioned between W(DCE) and DCE(W). The value of $[\mathrm{MPiCl_2}]$ in DCE(W) was calculated from the total amount of $\mathrm{MPiCl_2}$, found spectrophotometrically, using $K_A(\mathrm{MPiCl_2})$ in Table I. Resulting values of the partition coefficient, D/(mol^{-1} dm^3), were 1.46 ± 0.13 and 0.499 for $\mathrm{AgPiCl_2}$ and $\mathrm{CsPiCl_2}$, respectively.

Table III. Evaluation of $\Delta G^\circ_{\mathrm{tr}}(\mathrm{M^+} + \mathrm{PiCl_2^-})_{\mathrm{DCE(W)}\to\mathrm{W(DCE)}}$

$\mathrm{M^+}$	method^a	$\Delta G^\circ_{\mathrm{tr}}$/ (kJ mol^{-1})	$\mathrm{M^+}$	method^a	$\Delta G^\circ_{\mathrm{tr}}$/ (kJ mol^{-1})
$\mathrm{Ag^+}$	A	−38.1	$\mathrm{Ag^+}$	D	−38.9
$\mathrm{Ag^+}$	B	−39.8	$\mathrm{Cs^+}$	A	−37.9
$\mathrm{Ag^+}$	C	−38.7	$\mathrm{Cs^+}$	B	−34.5

^{a} A, from partitioning of uncomplexed $\mathrm{MPiCl_2}$ alone between DCE(W) and W(DCE); B, from solubility products of $\mathrm{MPiCl_2}$ in DCE(W) and W(DCE) in Table II; C, from extraction of 18-cr-6MPiCl$_2$, using eq 6, see text; D, from extraction of DB-18-cr-6MPiCl$_2$ using eq 6.

Partitioning of Complexed Metal Dichloropicrates. In this study, mixtures of $\mathrm{MPiCl_2}$ (2×10^{-4}–1×10^{-3} mol dm^{-3}) and 18-cr-6 (5×10^{-4}–7×10^{-3} mol dm^{-3}) or DB-18-cr-6 (0.002–0.020 mol dm^{-3}) in W(DCE) were shaken with equal volumes of DCE(W). Concentrations of the various species in the organic and aqueous phases were calculated using eqs 11 and 12 ($\mathrm{M^+} = \mathrm{Ag^+}$) and the charge balance relation

$$[\mathrm{LM^+}] + [\mathrm{M^+}] = [\mathrm{PiCl_2^-}] \quad (13)$$

The dichloropicrates were considered as completely dissociated in the aqueous phase. The small amount of $\mathrm{LM^+}$ present in this phase was taken into consideration, using the stability constants in water tabulated by Izatt et al. (*21*). Instead of employing Frensdoff's two-parameter regression method (*22*) for evaluation of K_{ex}, we used the experimental conductometric value of $K_A(\mathrm{LMPiCl_2})$ in Table II to calculate $[\mathrm{LM^+}]$ and $[\mathrm{LMPiCl_2}]$ in the organic phase. It appears that only a 1:1 18-cr-6Cs$^+$ complex is present under our experimental conditions. Frensdorff (*22*) reported the presence of $(\text{18-cr-6})_2\mathrm{Cs^+}$ in methanol solutions containing excess 18-cr-6.

Table II lists values of log K_{ex} (average deviation, 0–0.11 unit), $K_A(\mathrm{LMPiCl_2})$, and $K_f(\mathrm{LM^+})$, solvents being DCE and DCE(W). Several extraction experiments between water and benzene were carried out in the present study with the above dichloropicrates. The following values of log K_{ex} were obtained: 18-cr-6Na$^+$, 6.99; DB-18-cr-6Na$^+$, 5.05; 18-cr-6K$^+$, 8.47; and DB-18-cr-6K$^+$, 6.27.

Discussion

Sum of Gibbs Free Energies of Transfer of Uncomplexed Cation and Anion. Considering only the effect of dielectric permittivity, ϵ (Born effect), on each of the quantities on the right-hand side of eq 6, one concludes that K_{ex} is independent of ϵ of the two immiscible solvents. For simplicity, dielectric saturation effects were ignored. However, a large systematic increase in K_{ex} with ϵ was observed in the extraction of alkali-metal picrates between water and various nitrobenzene–toluene mixtures in the presence of DB-18-cr-6 (*4*). In fact, a good linear correlation was reported by Tôei et al. (*23*) between the distribution ratio of 18-cr-6KPi and Dimroth's E_T values of the organic solvents, excluding alcohols.

Agreement in values of $\Delta G^\circ_{\mathrm{tr}}(\mathrm{Ag^+}+\mathrm{PiCl_2^-})_{\mathrm{DCE(W)}\to\mathrm{W(DCE)}}$ in Table III attests to the validity of eq 6. The small difference of 3.4 kJ mol^{-1} in $\Delta G^\circ_{\mathrm{tr}}(\mathrm{Cs^+}+\mathrm{PiCl_2^-})_{\mathrm{DCE(W)}\to\mathrm{W(DCE)}}$ in Table III presumably corresponds to the free energy of hydration of solid $\mathrm{CsPiCl_2}$ to form the dihydrate.

Single Ion Free Energies of Transfer. As expected, nonelectrostatic free energies of transfer of ions from DCE into DCE(W) generally are small, indicative of, at most, a weak ionic hydration. The magnitude of $\Delta G^\circ_{\mathrm{tr}}(\mathrm{i})_{\mathrm{DCE(W)}\to\mathrm{PC}}$

Table IV. Gibbs Standard Free Energy of Transfer of Uncharged Ligands, Ion Pairs, and Single Ions on the Molar Scale ($kJ\ mol^{-1}$) at 298 K

species	DCE → DCE(W)	DCE(W) → PC	PC → W	DCE(W) → W	DCE → W
Ag^+	-1.22^a	-21.2^a	$-21.7,^b -18.0^c$	-42.9	-44.1
$AgPiCl_2$	-1.1^e	$-8.9_5{}^e$			
18-cr-6Ag^+		6.5_6	2.6_6	$9.2_3{}^j$	
DB-18-cr-6Ag^+		1.5_2	19.6^b	21.0^j	
Cs^+	4.0^g	-36.3	$-5.3_6,^b\ 1.7^c$	$-41.7^{i,j}$	$-37.7,^j -23.0^d$
18-cr-6Cs^+		2.8	7.6	10.4^j	
$PiCl_2^-$	-2.0^f	-16.0^f	19.8^f	3.8^f	1.8^f
Pi^-		-13.3	6.3	$-7.0^{h,j}$	-2.9^d
18-cr-6		7.2_7	-7.5_0	-0.2_3	
DB-18-cr-6		6.2_0	16.5_6	$22.76^{j,k}$	

[a] From K_f(C222Ag^+) in DCE, DCE(W) (Table II), or PC in eq 9. [b] Reference 9. [c] Abraham, M. H. *Monatsch. Chem.* **1979**, *110*, 517. [d] From electrostatic model;[25] see text. [e] $\Delta G^\circ_{tr}(MX)_{R\to S} = RT \ln 10\{\log[K_A(MX)_R/K_A(MX)_S]\} + \Delta G^\circ_{tr}(X^-)_{R\to S} + \Delta G^\circ_{tr}(M^+)_{R\to S}$. [f] $\Delta G^\circ_{tr}(PiCl_2^-)_{R\to S} = \Delta G^\circ_{tr}(Ag^+ + PiCl_2^-)_{S\to R} - \Delta G^\circ_{tr}(Ag^+)_{R\to S}$. [g] $\Delta G^\circ_{tr}(M^+)_{R\to S} = \Delta G^\circ_{tr}(M^+ + PiCl_2^-)_{R\to S} - \Delta G^\circ_{tr}(PiCl_2^-)_{R\to S}$. [h] From comparison of K_{ex} of 18-cr-6KPi with that of 18-cr-6$KPiCl_2$ using eq 6. [i] From partitioning of $CsPiCl_2$ between DCE(W) and W(DCE) (Table III); see text. [j] Transfer to W(DCE). [k] Reference 30.

of Cs^+, Pi^-, and $PiCl_2^-$ in Table IV, −36.3, −13.3, and −16.0 kJ mol^{-1}, is mainly attributed to the Born dielectric permittivity effect, −32.7, −13.8, and −13.8 kJ mol^{-1}, respectively. Ionic radii were taken as 0.169 (*24*), 0.40, and 0.40 nm. Silver ion appears to be nonelectrostatically solvated in DCE(W) to a considerable extent, the Born effect going from DCE(W) to PC amounting to −43.1 kJ mol^{-1} (r = 0.126 nm (*24*)) as compared to $\Delta G^\circ_{tr}(Ag^+)_{DCE(W)\to PC} = -21.2$ kJ mol^{-1} in Table IV.

We next consider free energies of transfer of ions from organic solvents to water. The reason that $\Delta G^\circ_{tr}(Cs^+)_{DCE\to W(DCE)}$ in Table IV is 10 kJ mol^{-1} more negative than that from DCE to pure water, as derived by Abraham and Liszi (*25*) from an electrostatic model in the organic solvent and hydration energy, could be due to a nonelectrostatic solvation effect on Cs^+ in W(DCE). An accurate evaluation of $\Delta G^\circ_{tr}(Cs^+,Ag^+)_{W(DCE)\to W}$ would entail an elaborate study, similar to that conducted by Popovych (*26*) between water and water–ethanol mixtures.

Several researchers note that the extractability of a potassium salt of a substituted phenoxide (*27*) or halide (*28*) decreases with increasing hydration energy of the anion. As expected, $\Delta G^\circ_{tr}(X^-)_{DCE(W)\to W}$ is in the order Cl^- < 4-nitrophenoxide < anilinonaphthalenesulfonate < Pi^- < $PiCl_2^-$, being −45.2 (*29*), −25.5 (*29*), −22.3 (*30*), −7.0, and 3.8 kJ mol^{-1} (Table IV). Values of ΔG°_{tr} of chloride, a typical "hard" ion, from $CHCl_3$ and CH_2Cl_2 to water, −63.3 and −70.4 kJ mol^{-1}, respectively, have been calculated from the empirical relation

$$\Delta G^\circ_{tr}(Cl^-)_{S\to W}/(kJ\ mol^{-1}) = (40.5 \pm 4.0) + (2.85 \pm 0.15)\Delta G^\circ_{distribution} \quad (14)$$

derived by Marcus et al. (*31*) for partitioning of DB-18-cr-6KCl between an organic solvent and water. Experimental values of $\Delta G^\circ_{distribution}$ are in ref 31. Dichloropicrate is hydrophobically solvated in water to a greater extent than picrate, $\Delta G^\circ_{tr}(PiCl_2^- - Pi^-)_{DCE(W)\to W} = 10.8$ kJ mol^{-1} (Table IV). This plays an important role in the favorable extractions of salts of substituted picrates in the presence of crown ethers. On the basis only of a smaller London dispersion interaction (*32*) anticipated between the organic solvent and $PiCl_2^-$ than with Pi^-, a negative value of $\Delta G^\circ_{tr}(PiCl_2^- - Pi^-)_{DCE(W)\to W}$ would be expected. Delocalization of the charge in $PiCl_2^-$ is suppressed as a consequence of the nitro groups being perpendicular to the ring.

Registry Numbers Supplied by Author. 1,2-Dichloroethane, 107-06-2; propylene carbonate, 108-32-7; dichloropicric acid, 19046-87-8; 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), 17455-13-9; 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (dibenzo-18-crown-6), 14187-32-7; 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (cryptand 2.2.2), 23978-09-8; silver perchlorate (hydrate), 14242-05-8.

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