probably carried out within the solid-phase range of this compound and have to be carefully reconsidered. Finally, the dearth of high-pressure thermodynamic data for organic solvents should be emphasized, as the field of high-pressure chemistry is rapidly expanding.

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Transfer Activity Coefficients of Alkali, Silver, Thallium(I), Chloride, and Picrate Ions between Methanol and Propylene Carbonate

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Solubility products of various salts in propylene carbonate (PC) have been determined in order to obtain transfer activity coefficients, ${}^{S_1}\gamma^{S_2}(M^+)$, of the ions mentioned in the title between methanol and PC. Values of log ${}^{M}\gamma^{PC}(M^+)$ are reported in Table III. A critical study of literature values of solubility products in PC has been made.

Introduction

In a recent study (*1*) we have reported transfer activity coefficients ${}^{M}\gamma^{S}(LM^+)$ at 25 °C of complexes of alkali, silver, and thallium(I) ions with dibenzo-18-crown-6 (DB-18) between methanol (M) on the one hand and water, acetonitrile (AN), propylene carbonte (PC), and dimethyl sulfoxide (Me_2SO) on the other. The extrathermodynamic assumption of Parker (*2*) that ${}^{M}\gamma^{S}(Ph_4As^+) = {}^{M}\gamma^{S}(BPh_4^-)$ was employed. The transfer activity coefficients of the various solvated cations, ${}^{M}\gamma^{S}(M^+)$, between methanol and the above solvents were required in order to obtain values of ${}^{M}\gamma^{S}(LM^+)$ in the various solvents. Such data are available in the literature. However, some discrepancy in literature values of ${}^{M}\gamma^{PC}(M^+)$ made it desirable to make an independent study of these values of the ions mentioned in the title. For this purpose it was necessary to determine the solubility products of silver tetraphenylborate, chloride, and picrate and thallium(I) tetraphenylborate in PC and of alkali chlorides in M, AN, and PC. From these data values of ${}^{M}\gamma^{PC}(Cl^-)$ and ${}^{M}\gamma^{PC}(Pi^-)$ were also obtained.

Experimental Section

Chemicals. Methanol was Fisher Spectroquality grade, distilled once over magnesium turnings. Acetonitrile was Aldrich Co. product, distilled over phosphorus pentoxide, while propylene carbonate was from Burdick and Jackson Laboratories, used without further purification. The water content of these solvents ranged from 0.003 to 0.01%. Silver chloride (*3*), perchlorate (*1*), and tetraphenylborate (*4*) and thallium(I) tetraphenylborate (*5*) had been used previously. Silver picrate was prepared from sodium picrate and silver nitrate in aqueous solution as described by Kolthoff, Lingane, and Larson (*6*). Tetraethylammonium tetraphenylborate was prepared by metathesis in aqueous solution of equimolar amounts of sodium tetraphenylborate and tetraethylammonium bromide. It was recrystallized from water. Tetraethylammonium (*7*), sodium (*5*) and potassium chlorides (*5*), and tetraethylammonium picrate (*8*), were also used previously. Lithium chloride was Mallinckrodt Reagent grade product recrystallized from an acetonitrile–water mixture (5:1). Rubidium and cesium chlorides were Ventron Co. puriss. grade and Fisher reagent grade products, respectively, and were not purified further. All salts were dried at 50 °C in vacuo.

Techniques. Solubility Determinations at 25.0 ± 0.1 °C. Saturated solutions of the alkali chlorides in methanol, acetonitrile, and propylene carbonate were prepared by stirring the finely divided salt suspension for 2 days and filtering. Total solubilities were determined by taking aliquots of the methanol or acetonitrile solutions to dryness (but not those of propylene carbonate), flooding with 50 volumes of methanol–water mixture (10:1), and titrating the residues potentiometrically with standard aqueous silver nitrate solution using a silver wire electrode. Saturated solutions of silver tetraphenylborate and chloride in PC were prepared by slowly adding, while stirring, 0.010 M silver perchlorate solution to 1.3×10^{-3}–3×10^{-3} M tetraethylammonium tetraphenylborate or chloride. In the chloride systems the mole ratio of Cl^- to Ag^+ was kept between 1 and 2 to avoid complete dissolution of silver chloride by complexation. The mixtures were initially opalescent; upon seeding with 5 mg of solid silver tetraphenylborate or chloride they became very turbid upon being stirred for 1 h. They were then stirred for 2 days and p*a*(Ag) values measured potentiometrically with a silver wire electrode. Stable potentials (to within ±1 mV) were attained after 10 min. Under these conditions supersaturation does not occur.

For the determination of the complexation constant $K^{f}(AgCl_2^-)$, solutions of silver perchlorate were added to tetraethylammonium chloride as described above, but in mole ratios of Cl:Ag ranging from 2:1 to 10:1, and p*a*(Ag) values of the resulting clear solutions measured within 15 min of preparation. All silver solutions were prepared and kept in dark containers.

Solubility products of thallium(I) tetraphenylborate and silver picrate in PC were estimated from p*a*(Tl) or p*a*(Ag) measurements in 0 to 4.3×10^{-3} M tetraethylammonium tetraphenylborate or picrate solutions saturated with thallium(I) tetraphenylborate or silver picrate, respectively. Measurements of p*a*(Tl) were made with a potassium ion selective electrode (Markson Co. Cat. No. 1002) conditioned in 5×10^{-4} M thallium(I) nitrate solution in PC. Total solubilities of silver picrate in absence and presence of tetraethylammonium picrate were determined by argentometric titration with potassium bromide in a similar way as with the alkali chlorides.

Instrumentation. The potentiometric cell and 0.010 M $AgClO_4$/Ag reference electrode used for p*a*(Ag) and p*a*(Tl)

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Table I. Solubility Products of Silver Tetraphenylborate, Picrate, Chloride, and Thallium(I) Tetraphenylborate in Propylene Carbonate

$c[Et_4NA]$	$c[AgClO_4]$	$[A^-]$	y	$pa(Ag)$ or $pa(Tl)$	$pK^{sp}(AgA)$ or $pK^{sp}(TlA)$	$K^f(AgCl_2^-)$
		$AgBPh_4$: $Et_4NBPh_4 + AgClO_4$				
1.34×10^{-3}	4.13×10^{-4}	9.27×10^{-4}	0.94	11.76	14.8_1	
2.26×10^{-3}	3.70×10^{-4}	1.89×10^{-3}	0.93	12.28	15.0_3	
3.60×10^{-3}	3.08×10^{-4}	3.29×10^{-3}	0.92	12.31	14.8_3	
					av. 14.9	
		$TlBPh_4$: $Et_4NBPh_4 + TlBPh_4$(Solid)				
0 ($TlBPh_4$ alone)		2.5×10^{-5}	0.99	4.41	8.8_2	
1.78×10^{-3}		$1.7_8 \times 10^{-3}$	0.93	5.80	8.5_8	
4.28×10^{-3}		$4.2_8 \times 10^{-3}$	0.90	6.15	8.5_6	
					av. 8.6_5	
		AgPi: Et_4NPi + AgPi(Solid)				
0 (AgPi alone)		$1.2_6 \times 10^{-3}$	0.94	2.92	5.8_5	
2.24×10^{-3}		$3.1 \times 10^{-3\,a}$	0.92	3.09	5.6_3	
4.47×10^{-3}		$5.1 \times 10^{-3\,a}$	0.91	3.25	5.5_8	
					av. 5.7	
		AgCl: $Et_4NCl + AgClO_4$ Solid AgCl Present				
3.10×10^{-3}	1.78×10^{-3}	$1.3_0 \times 10^{-4}$	0.94	16.2_6	20.1_8	
2.87×10^{-3}	2.31×10^{-3}	5.0×10^{-5}	0.97	15.8_2	20.1_4	
2.99×10^{-3}	2.00×10^{-3}	$8.1_7 \times 10^{-5}$	0.95	15.99	20.1_0	
					av. $20.1_4 \pm 0.0_4$	
		No Solid AgCl Present				
2.02×10^{-3}	0.901×10^{-4}	1.84×10^{-3}	0.93	19.64		$1.2_5 \times 10^{21}$
1.99×10^{-3}	2.66×10^{-4}	1.46×10^{-3}	0.93	19.13		$1.8_3 \times 10^{21}$
1.92×10^{-3}	5.98×10^{-4}	7.22×10^{-4}	0.93	18.27		(2.3×10^{21})
3.68×10^{-3}	1.64×10^{-4}	3.35×10^{-3}	0.92	19.83		1.1×10^{21}
3.62×10^{-3}	3.23×10^{-4}	2.98×10^{-3}	0.91	19.52		$1.3_3 \times 10^{21}$
3.48×10^{-3}	6.98×10^{-4}	2.09×10^{-3}	0.92	18.95		$1.5_4 \times 10^{21}$
3.33×10^{-3}	1.11×10^{-3}	1.11×10^{-3}	0.92	18.15		$1.4_0 \times 10^{21}$
						av. $1.4_0 \times 10^{21}$

[a] Ionic picrate concentration, calculated from the relation $c[Et_4N^+] + [Ag^+] = [Pi^-]$.

determinations have previously been described (*9*), as well as the conductance cell and salt bridge (*9*).

Results

Potentiometric Section. Solubility products (K^{sp}) of silver and thallium(I) tetraphenylborates and of silver chloride and picrate in propylene carbonate were obtained from measurements of $pa(Ag)$ or $pa(Tl)$ in tetraethylammonium tetraphenylborate, picrate, or chloride solutions saturated with the corresponding silver salt. Results are given in Table I, in which y denotes the Debye–Hückel activity coefficient. The three tetraethylammonium salts can be considered as completely dissociated (*10*). The constancy of K^{sp} values in Table I indicates negligible complexation, even though the silver ion is very poorly solvated in propylene carbonate.

From the total solubility of silver picrate, $4.8_1 \times 10^{-3}$ M (Table II), determined by potentiometric titration of the saturated solution of the salt in PC, $[AgPi]_{sat.} = 4.8 \times 10^{-3} - 1.2 \times 10^{-3} = 3.6 \times 10^{-3}$ M, and hence $K^d(AgPi) = 4.0 \times 10^{-4}$ is found.

The value of $pK^{sp}(AgBPh_4)$ of 14.9 found in the present study is at variance with 12.8 reported by Alexander and Parker (*11*) and 12.5 by Courtot-Coupez and L'Her (*12*). An explanation for this discrepancy is lacking. From the data in Table I, pK^{sp} of $TlBPh_4$ and AgPi are 8.6_5 and 5.7 ± 0.1. Silver chloride forms very stable complexes in propylene carbonate with chloride ion (*12, 13*). When chloride is in large excess over silver and solid AgCl is absent, $K^f(AgCl_2^-) \equiv [AgCl_2^-]/a(Ag^+)[Cl^-]^2y$ has been calculated by using eq 1 and 2, considering undisociated AgCl and $AgCl_3^{2-}$ as negligible. In Table I a constant value of

$$\Sigma[Ag^+] = [Ag^+] + [AgCl_2^-] \qquad (1)$$

$$\Sigma[Cl^-] = [Cl^-] + 2[AgCl_2^-] \qquad (2)$$

$K^f(AgCl_2^-)$ equal to 1.4×10^{21} is obtained, which is slightly larger than that of 0.73×10^{21} reported by Butler (*13*), who considered the presence of AgCl and $AgCl_3^{2-}$. Using Butler's value of $K^f(AgCl_3^{2-}) = 2.5 \times 10^{23}$ (overall formation constant) we calculate a ratio of $[AgCl_3^{2-}]/[AgCl_2^-] \sim 0.3$, when $\Sigma[Cl^-] = 3.3 \times 10^{-3}$ and $\Sigma[Ag^+] = 1.11 \times 10^{-3}$ M (last entry of Table I). When chloride is in excess over silver, but in the presence of solid AgCl, eq 3 was used to evaluate $[Cl^-]$, and hence $K^{sp}(AgCl)$, knowing $K^f(AgCl_2^-)$ and the experimentally determined values of $a(Ag^+)$, again neglecting AgCl and $AgCl_3^{2-}$. Equation

$$yK^f(AgCl_2^-)a(Ag^+)[Cl^-]^2 + [Cl^-] = \Sigma[Cl^-] - \Sigma[Ag^+] \qquad (3)$$

3 has been derived by Butler (*13*) from material balance relations for silver and chloride and the expression for $K^f(AgCl_2^-)$. The resulting value of $pK^{sp}(AgCl)$ equal to 20.1 in Table I agrees well with values in Table II quoted from the literature.

Conductometric Section. From the conductivity of saturated thallium(I) tetraphenylborate solution in PC, $1.22 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$, and $\Lambda_0(TlBPh_4) = 25.6$ (calculated from that in AN, using the Walden product), $[Tl^+]_{sat.} = 4.8_0 \times 10^{-5}$ M and $pK^{sp}(TlBPh_4) = 8.6_4$, in satisfactory agreement with the potentiometric value 8.8_2 (Table I).

Conductivities of saturated solutions of the alkali chlorides in methanol, acetonitrile, and propylene carbonate, total solubilities, dissociation constants, and solubility products calculated from these data are presented in Table II. When available, our values are compared with those in the literature. For estimation of ionic solubility from conductance data the following ionic mobilities were used: $\lambda_0(Li^+) = 73.3$ in AN (this work), 7.30 in PC (*14*); $\lambda_0(Na^+) = 9.45$ (*15*); $\lambda_0(K^+) = 11.97$ in PC (*14*); $\lambda_0(Rb^+) = 11.90$ in PC (*15*), 85.6 in AN (*16*); $\lambda_0(Cs^+) = 12.66$ in PC (*15*), 87.3 in AN (*16*); $\lambda_0(Cl^-) = 20.20$ in PC (*14*), 98.7 in AN (*16*). From comparison of total solubilities of RbCl and CsCl in PC with the corresponding ionic solubilities, calculated from the specific conductivities in Table II, it can be concluded that within ex-

Table II. Solubility of Chlorides and Silver Picrate in Acetonitrile, Propylene Carbonate, and Methanol at 25 °C

MCl	solvent	total solubility	conductance of satd soln	pK^d(MCl)	pK^{sp}(MCl)
LiCl	AN	2.5×10^{-2} [g]	3.88×10^{-4} [g]	3.6_0 [g]	5.3_1 [g]
	PC	$4.5_5 \times 10^{-2}$,[h] $4.1_7 \times 10^{-2}$ [g]	$2.0_6 \times 10^{-4}$ [g]	2.7_5,[j] 2.5_0 [g]	4.0_2,[j] 4.0_6 [g]
NaCl	AN	0.85×10^{-4} [c]	1.1×10^{-5} [c]	3.8[c]	8.3[c]
	PC	$1.4_6 \times 10^{-4}$ [h]	$3.0_8 \times 10^{-6}$,[g] $1.5_6 \times 10^{-6}$ [k]	*i*	(8.5),[k] 7.6_8,[h] 7.9_6 [g]
	M				2.1[b]
KCl	AN	$1.2_1 \times 10^{-4}$ [c]	$1.7_9 \times 10^{-5}$ [c]	~3[c]	7.2,[b] 8.0[c]
	PC	3.2×10^{-4},[k] $2.7_5 \times 10^{-4}$ [g] $4.1_9 \times 10^{-4}$,[h] 5×10^{-4} [k]	$8.7_8 \times 10^{-6}$ [g] $1.0_6 \times 10^{-5}$ [k]	*i*	6.9_1,[k] 7.1_4,[g] 6.7_8 [h]
	M	4.98×10^{-2} [c]			3.0,[b] 3.2,[c] 2.8_9 [d]
RbCl	AN		$4.1_6 \times 10^{-5}$ [g]		7.3_1 [g]
	PC	$7.1_4 \times 10^{-4}$ [g]	$2.2_7 \times 10^{-5}$ [g]	*i*	6.3_3 [g]
	M	$9.1_8 \times 10^{-2}$ [g]	$5.3_6 \times 10^{-3}$ [g]	$K_A = 0$ [l]	3.5_5 [d]
CsCl	AN		$8.2_5 \times 10^{-5}$ [g]	*i*	6.8,[b] 6.7_4 [g]
	PC	$1.3_6 \times 10^{-3}$ [g]	$4.7_3 \times 10^{-5}$ [g]	*i*	5.7_8 [g]
	M	0.160[h]	$8.4_5 \times 10^{-3}$ [g]		2.4[e] (3.4),[d] 2.6[b]
AgCl	AN				13.2,[b] 13.0[c]
	PC				20.0,[b] 20.0,[a] 20.1,[f] 19.8_7 [m]
	M				13.4[b]
TlCl	PC				12.3_7,[h] 12.4,[m] 11.4_5 [n]
	M		6.7×10^{-5} [c]		6.5[c]
AgPi	PC	4.8×10^{-3} [g]		4×10^{-4} [g]	5.7[g]
	M				3.4[o]

[a] Reference 12. [b] Alexander, R.; Parker, A. J. *J. Am. Chem. Soc.* 1972, *94*, 1148. Alexander, R.; Ko, E.; Mac, Y.; Parker, A. J. *Ibid.* 1967, *87*, 3703. [c] Reference 5, also: Chantooni, M. K., Jr.; Kolthoff, I. M. *J. Phys. Chem.* 1973, *77*, 1. [d] Chiang, F. Ph.D. Thesis, University of Minnesota, 1967. [e] Pavlopoulos, T.; Strehlow, H. *Z. Phys. Chem.* 1954, *202*, 474. [f] This work, from pa(Ag^+) in solutions of Et_4NCl saturated with AgCl. [g] This work, from conductance and total solubility of saturated solutions. [h] Cogley, C.; Butler, J.; Grunwald, E. *J. Phys. Chem.* 1971, *75*, 1477; complete dissociation assumed. [i] Electrolyte regarded as completely dissociated. [j] Reference 10. [k] Harris, W. Ph.D. Thesis, University of California, Berkeley, 1958. [l] Kay, L. *J. Am. Chem. Soc.* 1960, *82*, 2099. [m] Reference 13. [n] Matsuura, N.; Umenoto, K. *Bull. Soc. Chem. Jpn.* 1974 *47*, 1334. [o] Reference 6.

perimental error these electrolytes are completely dissociated in their saturated solutions in PC. The dissociation constant of lithium chloride in AN was found from a Fuoss and Kraus plot of conductance data at the following molarities of lithium chloride: $\Sigma[LiCl] = 6.07 \times 10^{-4}$, 1.19×10^{-3}, 1.74×10^{-3}, 3.69×10^{-3}, 5.36×10^{-3}, 8.58×10^{-3}, and 2.47×10^{-2} M, Λ = 81.3, 63.7, 50.0, 36.7, 33.9, 26.7, and 15.6, respectively. From the intercept, Λ_0(LiCl) = 172, as compared with the literature value of 168.0 (*16*).

Discussion

Two popular extrathermodynamic assumptions used in the evaluation of transfer activity coefficients of ions reported in the literature are the reasonable Grunwald (*17*) assumption $\gamma(Ph_4P^+) = \gamma(BPh_4^-)$ (or the similar assumption by Parker (*2*) that $\gamma(Ph_4As^+) = \gamma(BPh_4^-)$). On the other hand, Strehlow (*18*) assumes that γ(ferrocene) = γ(ferricinium), an assumption preferred by the French school. Recently, Takahashi et al. (*19*) proposed the reasonable assumption that $\gamma(R^+) = \gamma(R^-)$, R^+/R^- being a standard redox couple of very large ions with shielded charges. In a recent publication (*20*) evidence has been submitted that the Parker–Grunwald assumptions are most reliable. In Table III are compared values of log ${}^{M}\gamma^{PC}(M^+)$, log ${}^{M}\gamma^{PC}(Cl^-)$, and log ${}^{M}\gamma^{PC}(Pi^-)$ based on the tetraphenylborate and ferrocene assumptions. Omitting log ${}^{M}\gamma^{PC}(Tl^+)$, we find a difference 1.3 ± 0.2 in log ${}^{M}\gamma^{PC}(M^+)$ based on these two assumptions. This difference has been reported earlier by us (*5*) for Ag^+ between methanol and several dipolar aprotic solvents.

Consider now the transfer of Ag^+ between two aprotic solvents AN and PC. By use of the value of p$K^{sp}(AgBPh_4)$ = 14.9 in PC, found in the present study, the following values of log ${}^{AN}\gamma^{PC}(Ag^+)$ are obtained: 7.7 (tetraphenylborate assumption); 9.5 ($\gamma(Ph_4As^+) = \gamma(Ph_4C)$ assumption (*21*)); 7.4 ($\gamma(Ph_4B^-) = \gamma(Ph_4C)$ assumption (*21*)); 6.0 ($\gamma_{\pm} = \gamma(CH_3I)$ assumption (*21*)); 7.6 (*21*), 7.5 (*22*) (ferrocene assumption); 6.9 (negligible liquid junction potential assumption (*21*)) and 7.2 (R^-/R^+ reference couple (*19*)). In general, the assumptions considered to be the most reliable yield values of log ${}^{AN}\gamma^{PC}(Ag^+)$ in satisfactory agreement.

Table III. Comparison of Values of log ${}^{M}\gamma^{PC}(M^+)$ Derived from Ferrocene and Tetraphenylborate Assumptions

	potential $E°(M) - E°(Fc)$, V		log ${}^{M}\gamma^{PC}(M^+)$		
M^+	in MeOH[a]	in PC[b]	$\gamma(BPh_4^-) = \gamma(Ph_4As^+)$	ferrocene	diff
Ph_4As^+			−2.2[c]		
Li^+		−3.265			
Na^+	−3.229	−3.050	$+1.5_4$ [d]	$+3.0_3$	+1.5
K^+	−3.422	−3.354	-0.1_6 [d]	$+1.1_5$	+1.3
Rb^+	−3.413	−3.379	-0.4_8 [d]	$+0.5_7$	+1.1
Cs^+		−3.391	-0.6_6 [d]		
Tl^+	−0.880	−0.767	$+1.0_5$ [e]	$+1.9_1$	+0.9
Ag^+	+0.0263	+0.501	+2.6[e]	$+4.0_3$	+1.4
Cl^-			+4.1		
Pi^-			−0.3		

[a] Compiled from standard potential data of: Buckley, P.; Hartley, H. *Philos. Mag.* 1929, *8*, 320; Brauer, K.; Strehlow, H. *Z. Phys. Chem. (Wiesbaden)* 1958, *17*, 346; and the value of $E°(Ag) - E°(Fc)$ = +0.263 in ref 21. [b] L'Her, M.; Courtot-Coupez, J. *Bull. Soc. Chim. Fr.* 1972, 3645. [c] Reference 11. [d] From log ${}^{M}\gamma^{PC}(Ag^+)$ = 2.6 (this work), log ${}^{M}\gamma^{AN}(M^+)$, log ${}^{M}\gamma^{AN}(Cl^-)$, ${}^{PC}\Delta^{AN}$pK^{sp}(MCl) in eq 4; see text. [e] From log ${}^{M}\gamma^{PC}(BPh_4^-)$, p$K^{sp}(AgBPh_4)$ or p$K^{sp}(TlBPh_4)$ in PC in Table I, and in methanol, from ref 5.

Since the alkali picrates, tetraphenylborates, and some chlorides are readily soluble in methanol and/or PC, no reliable values of their K^{sp} are found in the literature. For this reason, an indirect route involving the solubility products of the alkali chlorides in AN was used (eq 4) to calculate values of log ${}^{M}\gamma^{PC}(M^+)$ listed in Table III, based on the tetraphenylborate assumption. Values of log ${}^{M}\gamma^{AN}(M^+)$ and log ${}^{M}\gamma^{AN}(Cl^-)$ = 5.2

$$\log {}^{M}\gamma^{PC}(M^+) = \log {}^{M}\gamma^{AN}(M^+) + {}^{PC}\Delta^{AN}pK^{sp}(MCl) + \log {}^{M}\gamma^{AN}(Cl^-) - {}^{PC}\Delta^{M}pK^{sp}(AgCl) + \log {}^{M}\gamma^{PC}(Ag^+) \quad (4)$$

were taken from a previous publication (*5*), while pK^{sp}(MCl) and pK^{sp}(AgCl) in the solvents designated are from Table II. With the exception of pK^{sp}(AgCl) in methanol, values of the above solubility products used were from this laboratory. Transfer activity coefficients based on the ferrocene assumption in Table

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III were calculated in the conventional way from values of $E^\circ(M) - E^\circ(Fc)$. On the basis of both assumptions, chloride ion is, as expected, considerably more solvated in methanol than in propylene carbonate. For anions with a localized charge this is primarily due to hydrogen bonding of the alcohol to these anions. Ion–dipole interaction between the anion and an aprotic solvent is impeded by steric shielding of the positive end of the dipole in many aprotic solvents. On the other hand, when the charge is highly delocalized, as in the lipophilic picrate ion, a negligible free energy of transfer has been found between methanol and aprotic solvents (*5*), PC being a typical aprotic solvent. It is of interest to report the transfer activity coefficient of M^+ (except, of course, Ag^+) between the two aprotic solvents AN and PC. Values of $\log {}^{AN}\gamma^{PC}(M^+)$ are –0.1, +0.6, +0.2, +0.1, +0.1, and +0.1 for Li^+, Na^+, K^+, Rb^+, Cs^+, and Tl^+.

Considering the Born effect, which attempts to take into account the solvent's dielectric constant, the values of $\log {}^{AN}\gamma^{PC}(M^+)$ become +2.5, +2.2, +1.3, +1.1, +1.0, and +1.1, respectively, while those of $\log {}^{M}\gamma^{PC}(M^+)$ become +3.5, +1.2, $+0.7_4$, $+0.4_2$, +1.3, and +4.0. In the latter series M^+ is Na^+, K^+, Rb^+, Cs^+, Tl^+, and Ag^+. Dielectric constants (*23*) of 32.7, 36.0, and 64.4 of M, AN, and PC, respectively, and Pauling's (*24*) crystallographic radii were used. It appears that, corrected for the Born effect, all the alkali ions and Tl^+, particularly Li^+ and Na^+, are considerably more solvated in M or AN than in PC. This is the opposite of what would be expected on the basis of ion–dipole interaction, the dipole moments (*23*) of PC, AN, and M being 4.98, 3.92, and 1.70 D, respectively. Evidently, nonelectric (neutral) ion–solvent interactions play an important role.

The species $AgCl_2^-$ is solvated to about the same extent in nitromethane, sulfolane, and dimethyl sulfoxide as in PC but is solvated to a greater extent in M and AN. In the order given, values of $\log {}^{PC}\gamma^{S}(AgCl_2^-)$ are +0.2 (*25*), –0.8 (*26*), +0.2, +1.9, and +1.9. As compared to Ag^+ and Cl^-, which are hydrophilic, $AgCl_2^-$ has considerable lipophilic character and is a soft anion as compared to the hard chloride ion, $\log {}^{PC}\gamma^{M}(AgCl_2^-) - \log {}^{PC}\gamma^{M}(Cl^-)$ being $1.9 + 4.1 = 6.0$. As a matter of fact, $AgCl_2^-$ appears to be more lipophilic than the picrate ion, $\log {}^{PC}\gamma^{M}(Pi^-)$ being +0.3 as compared to $\log {}^{PC}\gamma^{M}(AgCl_2^-)$ of +1.9. The difference between log γ values of two ions is independent of the assumption on which γ values are based.

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Mutual Diffusion Coefficients of $BaCl_2$–H_2O and KCl–H_2O at 25 °C from Rayleigh Interferometry

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The volume-fixed mutual diffusion coefficients of $BaCl_2$–H_2O and KCl–H_2O have been measured to an accuracy of 0.1–0.2%, from dilute solutions to near saturation, using free-diffusion Rayleigh interferometry. These diffusion coefficients are compared to other available diffusion data for these systems, measured by the conductometric and optical methods. The new data extend previously available optical results to higher and lower concentrations and confirm that the diffusion coefficients of $BaCl_2$–H_2O are unusually low, relative to the other alkaline earth chlorides, at moderate and high concentrations. The effect of cation hydration on the diffusion coefficients of alkali and alkaline earth chloride solutions is briefly discussed.

Introduction

Mixing of chemical species by diffusion is important in a variety of natural phenomena including some geochemical processes.[1] To understand these phenomena requires the use of accurate diffusion coefficient data. Although determinations of differential mutual diffusion coefficients have been made since the late 1940's, accurate diffusion data are available for relatively few systems. One reason for the scarcity of such data involves the large amount of effort involved in performing the experiments and, for optical methods, in the subsequent reading of the photographic records.

To supplement the available diffusion coefficient data, it is desirable to develop methods of approximating data for binary and for mixed salt systems. Very accurate data are required for a number of representative systems in order to correlate

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