

Thermodynamics of Ion-Solvent Interactions

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1 Introduction

The interaction energies of dissolved ions with the surrounding solvent are large, comparable to the lattice energies of ionic crystals. Changes in these ion-solvent interactions on transfer of electrolytes between solvents are smaller, but are sufficiently large to cause dramatic changes in chemical reactions involving ions.¹ These changes in ionic solvation have important applications in such diverse areas as organic² and inorganic³ synthesis, studies of reaction mechanisms,^{4,5} non-aqueous battery technology,⁶ and the extraction and purification of metals,⁷ among others.

In this article the changes in the thermodynamics of ionic solvation with changes in the solvent system are discussed. In addition, the relevance of ion-solvent molecule interactions in the gas phase to ionic solvation and the significance of various theories of ion-solvent interactions are considered.

2 Experimental Data

Thermodynamic studies have been reported for a wide range of electrolytes in an enormous number of single component and binary mixed solvent systems, and considerable selectivity has been required in compiling the data listed below. Thus data are listed only for solvent systems for which extensive results have been reported and which can be considered to be broadly representative of the different types of solvent systems commonly studied.

Tables 1, 2, and 3 list the standard free energies, ΔG°_s , enthalpies, ΔH°_s , and entropies, ΔS°_s (as $-298\Delta S^\circ_s$), of solution of electrolytes in water; and their free energies, ΔG°_{tr} , enthalpies, ΔH°_{tr} , and entropies, ΔS°_{tr} (as $-298\Delta S^\circ_{tr}$), of transfer from water into a variety of single-component solvent systems. Tables 4,

¹ A. J. Parker, *Quart. Rev.*, 1962, **16**, 163.

² J. E. Shaw, D. C. Kunnerth, and S. B. Swanson, *J. Org. Chem.*, 1976, **41**, 732.

³ M. Muto, T. Baba, and H. Yoneda, *Bull. Chem. Soc. Japan*, 1968, **41**, 2918.

⁴ E. Buncel and H. Wilson, *Adv. Phys. Org. Chem.*, 1977, **14**, 133.

⁵ A. J. Parker, *Chemtech*, 1971, **1**, 297.

⁶ (a) M. Salomon, Proceedings of the Power Sources Symposium, 1974, vol. **26**, p. 71; (b) R. J. Jasinski, 'High Energy Batteries', Plenum Press, New York, 1967.

⁷ D. M. Muir, A. J. Parker, J. H. Sharp, and W. E. Waghorne, *Hydrometallurgy*, 1975, **1**, 61, 155.

Table 1 Standard free energies of transfer (ΔG_{tr}°) of 1:1 electrolytes from water to non-aqueous solvents^a at 25 °C
 $\Delta G_{tr}^\circ/\text{kcal mol}^{-1}$ (molar scale)^b

Salt	$\Delta G_{tr}^\circ/\text{kcal mol}^{-1}$ (molar scale) ^b						
	H ₂ O (ΔG_{s}°) ^{c,d}	MeOH	HCONH ₂	DMF	DMSO	PC	MeCN
LiCl	-9.9	4.0 ^e	1.0 ^f	(7.4) ^g	4.8 ^h	14.8 ^{i,j}	15.8 ^k
LiBr	-13.6				2.4 ^l	12.8 ^t	
LiI	-18.6	2.7 ^m			0.8 ^l	10.0 ^k	
NaCl	-2.15	5.2 ^{e,m}	1.4 ^f	8.8 ⁿ	6.1 ⁿ	12.8 ^j	13.4 ⁿ
NaBr	-4.1	4.7 ^{e,m}					11.2 ^k
KCl	-1.23	5.5 ^e	2.2 ^f	8.7 ⁿ		10.7 ^j	12.0 ⁿ
KBr	-1.41	4.9 ^m	0.7 ^f	5.4 ⁿ	3.2 ^o		9.2 ^k
KI	-2.79	4.1 ^m	0.7 ^f			5.0 ^{t,j}	6.3 ^{k,p}
KClO ₄	2.72 ^q	3.8 ^r	-1.6 ^s	-0.5 ^p			3.0 ^{n,p}
KBPh ₄	10.26 ^{t,u}	-3.3 ^{t,u}	-6.4 ^o			(-7.6) ^v	-6.1 ⁿ
RbCl	-2.0	5.8 ^e	2.0 ^f			(9.9) ^v	12.0 ^k
RbBr	-1.64	5.3 ⁿ		5.3 ⁿ	3.6 ^w		9.0 ^k
RbClO ₄	3.45 ^{q,r}	4.0 ^r	-1.6 ^s	-0.5 ^p			2.7 ^{n,p}
RbBPh ₄	11.6 ^x	-3.4 ^u					-6.3 ^x
CsBr	-0.38	5.1 ^k	1.0 ^f	5.3 ^o	3.0 ^w	(7.3) ^v	8.3 ⁿ
CsI	-0.06	4.1 ^k		2.4 ^o		(4.2) ^v	5.6 ^k
CsClO ₄	3.25 ^{q,r}	3.9 ^r	-1.3 ^s				2.2 ⁿ
CsBPh ₄	11.99 ^x	-3.5 ^o				-7.1 ^y	-6.7 ^x
AgCl	13.30	5.0 ^o	-0.4 ^o	6.9 ^o	1.4 ^{o,z,aa}	13.8 ^{o,bb}	4.5 ^{o,z,cc}
AgBr	16.74	4.5 ^o	-1.1 ^o	4.1 ^{o,dd}	-1.7 ^{o,aa}	11.4 ^{o,bb}	2.0 ^{z,cc}
AgI	21.82	3.6 ^o	-2.0 ^o	0.6 ^{o,dd}	-5.6 ^{o,aa}	8.0 ^{o,bb}	
AgN ₃	11.7	4.0 ^o	-1.0 ^o	3.7 ^o		10.8 ^o	1.7 ^o
AgOAc	3.70	5.6 ^{n,o}			6.4 ^{z,aa}		8.2 ^{n,z}

AgBPh ₄	23.4	-3.8 ⁿ	-9.3 ^o	-13.4 ^{n,o}	-16.8 ^{n,o}	-6.0 ^{o,bb}	-13.1 ^{n,o}
TlCl	5.09	3.8 ⁿ			4.2 ^{n,ee}		12.9 ^x
TlBr	7.41				1.1 ^{ee}		10.2 ^x
Me ₄ NI	2.33 ^p	3.6 ^p		3.1 ^p	1.5 ^p		3.8 ^p
Et ₄ NI	1.14 ^p	1.9 ^p		2.6 ^p	2.1 ^p		2.5 ^p
Pr ₄ NI	2.13 ^p	-0.3 ^p		0.2 ^p			0.2 ^p
Ph ₄ AsI	6.95 ^o	-3.9 ^o	-4.3 ^o	-4.4 ^o		-4.7 ^o	-3.3 ^o
Ph ₄ AsClO ₄	11.44 ⁿ	-4.2 ⁿ					-6.6 ⁿ
Ph ₄ AsBPh ₄	23.5 ^{ff}	-11.2 ^o	-11.3 ^o	-18.3 ^{n,o,gg}	-17.8 ^{n,o,gg}	-17.2 ^o	-15.6 ^{o,gg}

(a) Abbreviations are: DMF, dimethylformamide; DMSO, dimethyl sulphoxide; PC, propylene carbonate (1,2-propanediol carbonate); (b) 1 cal = 4.184 J; (c) W. M. Latimer, 'Oxidation Potentials', 2nd edn., Prentice Hall, New Jersey; (d) F. D. Rossini *et al.*, U.S. Nat. Bureau of Standards, Circular 500 and supp. notes 270-1 to 270-3; (e) ref. 22(a); (f) E. Luksha, Ph.D. Thesis, Univ of Vermont, 1965; (g) est. from solubility in R. S. Kittila, 'DMF-Chemical Uses', E. I. du Pont de Nemours and Co., Wilmington, Del., 1967, 226; (h) ref. 21; (i) ref. 19(a); (j) ref. 12; (k) J. Pavlopoulos and H. Strehlow, *Z. Phys. Chem.*, 1954, 202, 474; (l) ref. 19(b); (m) ref. 18; (n) ref. 9; (o) ref. 8; (p) ref. 10; (q) W. B. Guenther, *J. Amer. Chem. Soc.*, 1969, 91, 7619; (r) ref. 15; (s) H. J. M. Denessen, C. L. De Ligny, and A. G. Remijns, *J. Electroanal. Chem.*, 1974, 51, 215; (t) ref. 11; (u) O. Popovych, *Anal. Chem.*, 1966, 38, 558; (v) estimated from data in ref. 28, 29; (w) from data in ref. 9; (x) O. Popovych, A. Gibofsky, and D. H. Berne, *Anal. Chem.*, 1972, 44, 811; (y) ref. 38; (z) M. K. Chantooni and I. M. Kolthoff, *J. Phys. Chem.*, 1973, 77, 1; (aa) M. Le Demezet, *Bull. Soc. Chim. Fr.*, 1970, 29, 21; (bb) ref. 13; (cc) D. C. Luehrs, R. T. Iwamoto, and J. Kleinberg, *Inorg. Chem.*, 1966, 5, 201; (dd) M. Breant, C. Buisson, M. Porteix, J. L. Sue, and J. P. Terrat, *J. Electroanal. Chem.*, 1970, 24, 409; (ee) J. Courtoi-Coupez, M. Le Demezet, A. Laouenan, and C. Maded, *J. Electroanal. Chem.*, 1971, 29, 21; (ff) ref. 44; (gg) J. I. Kim, *J. Phys. Chem.*, 1978, 82, 191.

Table 2 Enthalpies of transfer (ΔH_{tr}°) of 1:1 electrolytes from water to non-aqueous solvents^a at 25°C

Salt	$\Delta H_{tr}/\text{kcal mol}^{-1b}$							
	H ₂ O (ΔH_f) ^c	MeOH	HCONH ₂	DMF	DMSO	PC	MeCN	
LiCl	-8.85	-3.20 ^d	-0.3 ^e	-2.8 ^{f,g,h}	-2.1 ^{f,i}			
LiI	-15.13		-3.2 ^e	-10.9 ^{f,g}	-9.3 ^{f,i}	0.1 ^d	-1.5 ^f	
NaF	0.22		1.2 ^e					
NaCl	0.93	-2.83 ^f	-3.0 ^e		-2.6 ⁱ			
NaBr	-0.14	-3.91 ^d	-4.0 ^e	-7.2 ^{g,k}	-6.0 ⁱ			
NaI	-1.80	-5.27 ^{d,f}	-5.6 ^{i,m}	-11.4 ^{h,n}	-9.7 ^{i,o,p}	-3.2 ^d	-5.0 ^{j,m,q}	
NaClO ₄	3.32	-5.9 ^f		-13.3 ^f	-11.2 ^f	-6.4 ^d	-7.5 ^q	
NaBPh ₄	-4.78 ^{d,o}	-5.28 ^d	-4.0 ^m	-12.7 ^{d,n}	-9.5 ^o	-5.9 ^d	-5.6 ^m	
KCl	4.12	-2.55 ^d	-3.30 ^e		-4.3 ⁱ			
KBr	4.75	-3.41 ^d	-5.0 ^e	-8.4 ^{f,k}	-7.5 ^{f,i}	-2.3 ^r		
KI	4.86	-5.01 ^d	-5.9 ⁱ	-12.8 ^{f,h}	-11.3 ^{f,i}		-7.3 ^{i,q}	
RbCl	4.13	-1.93 ^d	-3.48 ^{i,s}		-4.9 ⁱ			
RbI	6.00		-5.8 ⁱ	-12.6 ^h	-12.0 ⁱ	-6.8 ^r	-7.9 ^q	
RbBPh ₄	11.73 ^d	-4.25 ^d		-13.7 ^d		-9.3 ^d		
CsCl	4.25	-1.37 ^d	-3.5 ^{i,s}		-3.8 ⁱ			
CsI	7.99		-6.2 ⁱ	-12.2 ^h	-10.9 ⁱ	-7.2 ^r	-8.0 ^q	
AgBr	20.2			-8.4 ^m	-11.1 ^m	1.0 ^m	-10.9 ^m	
Ph ₄ AsCl	-2.57 ^d	1.59 ^d		0.4 ^d	1.4 ^d	2.8 ^d		
Ph ₄ AsBr	1.80 ^d		-0.5 ^m		-1.8 ^d	0.0 ^d	-0.5 ^m	
Ph ₄ AsI	8.28 ^o		-1.9 ^m		-5.5 ⁿ		-4.1 ^m	
Me ₄ NI	10.07	-0.33 ^d	-2.2 ⁱ	-7.6 ^d	-6.8 ^d	-4.7 ^d	-5.5 ^q	
Et ₄ NI	6.72	1.53 ^d	-0.4 ⁱ	-7.2 ^d	-1.9 ^o	-0.6 ^d	-2.1 ^q	
Pr ₄ NI	2.76	3.31 ^d	2.3 ⁱ	-3.2 ^d	-0.8 ^d	2.0 ^d	0.6 ^q	
Bu ₄ NI	3.90	4.67 ^d	4.5 ⁱ	-0.8 ^d	1.0 ^d	4.0 ^d	2.6 ^q	

(a) Abbrev. as in Table 1; (b) 1 cal = 4.184J; (c) Enthalpies of solution of electrolytes in water—V. B. Parker, Thermal Properties of Aqueous Univalent Electrolytes, U.S. National Bureau of Standards, NSRDS-NBS2, Washington, D.C., 1965; (d) ref. 41; (e) G. Somsen and J. Coops, *Rec. Trav. Chim.*, 1965, **84**, 985; (f) R. Fuchs, J. L. Bear, and R. F. Rodewald, *J. Amer. Chem. Soc.*, 1969, **91**, 5797; (g) Y. A. Tsai and C. M. Criss, *J. Chem. Eng. Data*, 1973, **18**, 51; (h) ref. 34; (i) A. F. Vorob'ev, A. S. Monastkova, and I. P. Padunova, Conf. Int. Thermo. Chim CR, ed. J. Rougerol and R. Sabbah, 1975, 29; (j) Y.-S. Choi and C. M. Criss, *J. Chem. Eng. Data*, 1977, **22**, 297; (k) D. S. Gill, J. P. Singla, and R. C. Paul, *J.C.S. Dalton*, 1972, 522; (l) D. V. S. Jain, B. S. Lark, S. P. Kochan, and V. P. Gupta, *Indian J. Chem.*, 1969, **7**, 256; (m) ref. 44; (n) F. Rallo and F. Rodante, *Gazz. Chim. Ital.*, 1972, **102**, 56; (o) ref. 36; (p) ref. 35; (q) ref. 10; (r) calc. from data in (d); (s) L. Weeda and G. Somsen, *Rec. Trav. Chim.*, 1967, **86**, 263; (t) C. de Visser and G. Somsen, *Rec. Trav. Chim.*, 1971, **90**, 1129 and (c).

Table 3 Entropies of transfer (ΔS_{tr}°)^a of 1:1 electrolytes from water to non-aqueous solvents^b at 25°C

Salt	$298\Delta S_{tr}^{\circ}/\text{kcal mol}^{-1}$ (molar scale) ^c							
	H ₂ O	MeOH	HCONH ₂	DMF	DMSO	PC	MeCN	
LiCl	0.0	-7.2	-1.3	-10.2	-7.5	-7.2	-10.2	
NaCl	0.0	-8.1	-4.5	-12.4	-8.8	-9.0	-11.5	
NaBr	0.0	-8.6	-4.8	-12.8	-9.1	-9.7	-12.1	
NaI	0.0	-9.2	-5.9	-14.1	-9.4	-10.4	-12.8	
KCl	0.0	-8.1	-6.0	-13.6	-10.5	-9.8	-12.2	
KClO ₄	0.0	-8.2	-6.8	-14.1			-12.5	
RbCl	0.0	-7.7	-5.5	-13.5	-11.5	-9.8	-12.7	
CsCl	0.0	-6.8	-5.8	-13.0	-9.8	-9.9	-12.2	
AgBr	0.0	-8.4		-12.5	-12.8	-10.4	-12.9	
Me ₄ NI	0.0	-3.6	-4.5	-10.3	-8.2		-9.4	
Et ₄ NI	0.0	-0.3		-5.8	-4.0		-3.1	
Pr ₄ NI	0.0	3.6	3.0	-1.0			0.8	
Ph ₄ AsI	0.0	3.0	2.4	-3.3	-0.5	0.6	-0.9	
KBPh ₄	0.0	-1.5	1.8	-2.6	-0.9	-1.1	-1.9	
Ph ₄ AsBPh ₄	0.0	10.6	11.5	9.6	12.5	10.8	10.9	

(a) Values obtained by the application of equation (1) to data in Tables 1 and 2; (b) Abbrev. as in Table 1; (c) 1 cal = 4.184J.

Table 4 Standard free energies (ΔG_{tr}°), enthalpies (ΔH_{tr}°), and entropies (ΔS_{tr}°) of transfer of electrolytes from water to mixtures of water and acetonitrile at 25°C

Salt	Wt % MeCN	ϕ_{MeCN}^a	0.2	0.4	0.6	0.8	0.9	0.95	1.0	
	7.94	0.1	16.4	34.4	54.1	75.8	87.6	93.8	100	
			$\Delta G_{tr}^\circ/\text{kcal mol}^{-1}$ (molar scale) ^b							
LiCl ^{c,f}	0.30	0.69	1.31	2.31	4.28	7.40	10.0	15.8 ^{d,f,g}		
NaCl ^{c,f}	0.27	0.51	1.24	2.23	3.94	7.02	9.74	13.4 ^{d,h}		
KCl ^{c,f}	0.19	0.45	1.13	2.09	3.59	6.28	8.68	12.0 ^{d,i}		
RbCl ^{c,j,k}	0.18	0.38	1.12	2.07	3.87			12.0 ^{d,l}		
CsCl ^{c,j,k}	0.19	0.37	0.89	1.60	3.48	6.08	8.41	11.6 ^{d,h}		
AgCl ^{d,k,m}	-1.0	-1.4	-2.0	-2.1	-0.5	1.3	2.4	3.9		
CuCl ^{e,n}	-5.6	-7.7	-8.6	-9.2	-7.8	-6.0	-4.9	-3.4		
CuCl ₂ ^{e,n}	1.3	2.0	3.2	4.3	9.2	14.8	20.4	29.4		
FeCl ₂ ^{e,n}	1.4	2.1	3.2	4.0	9.6	16.9	23.2	39.8		
FeCl ₃ ^{e,n}	1.4	3.1	4.7	6.0	14.0	25.5	34.4	77.9		
KBr ^{c,f}	0.09	0.29	0.82	1.60	3.06	5.57	7.28	9.2 ^{d,h}		
AgBr ^{d,f}	-1.40	-1.92	-2.70	-2.65	-2.00	-1.00	0.30	2.3 ^{d,h}		
Bu ₄ NBr ^{d,p,k}	-0.5	-0.3	-2.2	-3.7	-3.5	-2.8		-0.3 ^{d,p}		
KI ^{c,f}	0.03	0.05	0.30	0.81	1.94	3.19	4.20	6.4 ^{d,o}		
AgI ^{d,f}	-1.40	-2.25	-3.00	-3.20	-3.20	-2.40	-1.80	-1.0 ^d		
Ph ₄ AsI ^{d,f}	-0.9	-2.3	-4.0	-4.7	-4.9	-4.4	-3.9	-3.3 ^{d,i}		
KBPh ₄ ^{d,f}	-0.8	-1.8	-4.0	-6.0	-6.5	-6.4	-6.2	-6.0 ^{d,h}		
			$\Delta H_{tr}^\circ/\text{kcal mol}^{-1b}$							
LiCl ^{e,f}		-0.5	-0.9	-1.8	-2.5	-4.6	-7.0	4.9 ^{d,r}		
NaCl ^{d,f}		-0.5	-1.0	-1.5	-3.0	-4.5		1.6 ^{d,s}		
KCl ^{d,f}		-0.9	-1.6	-2.7	-4.0			-0.7 ^{d,s}		

Table 5 Standard free energies (ΔG°_{tr}), enthalpies (ΔH°_{tr}), and entropies (ΔS°_{tr}) of transfer of electrolytes from water to mixtures of water and methanol at 25°C

Salt	Wt % MeOH	ϕ_{MeOH}^a	$\Delta G^\circ_{tr}/\text{kcal mol}^{-1}$ (molar scale) ^b										
			10	20	40	50	60	80	90	100			
HCl ^{c,f}		0.123	0.240	0.457	0.558	0.654	0.835	0.919	1.40				
LiCl ^{c,f}		0.31	0.62	1.27	0.84	1.04	1.93	2.75	5.64				
NaCl ^{c,f}		0.43	0.88	1.79	2.29	2.79	3.97	4.60	3.96				
KCl ^{c,f}		0.43	0.88	1.80		2.87	4.17		5.20				
RbCl ^{c,f}		0.43	0.86	1.75	2.28	2.81	4.17		5.50				
CsCl ^{c,f}		0.40	0.80	1.65	2.14	2.68	4.03		5.60				
AgCl ^{c,h}		0.35	0.69	1.44 [†]	1.95 ^{†,j}				5.7 ^{e,g}				
LiFe ₃ ^g						2.3 [‡]	2.6 [‡]	3.6 [‡]	4.0				
NaF ^{e,g}				2.1 [‡]		3.5 [‡]	4.8 [‡]	5.4 [‡]	5.4				
HBr ^{c,f}		0.13	0.22	0.40	0.51	0.68	1.46	2.27	5.12				
NaBr ^{c,t}		0.38	0.77	1.54	1.96	2.44	3.51	4.12	4.61				
AgBr ^{c,m}		0.33	0.52	0.95 [‡]	1.27 [‡]				4.50 ^k				
HI ^{c,f}		0.06	0.08	0.00	0.05	0.12	0.68	1.46	4.09				
NaI ^{c,t}		0.31	0.63	1.16	1.49	1.86	2.70	3.21	3.75				
AgI ^{c,n}		0.34	0.69	0.53 [‡]	0.74 [‡]				3.60 ^k				
KClO ₄ ^{c,o}		0.27		0.99 [‡]				2.94 [‡]	3.48				
RbClO ₄ ^{c,o}		0.33		1.05 [‡]				3.07 [‡]	3.69				
Me ₄ NCIO ₄ ^{c,o}		0.18		0.31 [‡]				2.15 [‡]	3.06				
n-Pr ₄ NCIO ₄ ^{c,o}		-0.23		-1.04 [‡]				-1.29	-0.82				

$\Delta H_{tr}^{\circ}/\text{kcal mol}^{-1b}$

LiCl ^{e,p}	0.29	0.39	0.16	-0.60	-2.05	-3.20 ^a
NaCl ^{e,p}	0.44	0.74	0.78	0.52	-0.73	-2.83 ^a
KCl ^{e,p}	0.39	0.59	0.53	0.18	-0.66	-2.55 ^a
RbCl ^{e,p}	0.39	0.56	0.43	0.07	-0.52	-1.93 ^a
CsCl ^{e,p}	0.41	0.53	0.30	-0.10	-0.49	-1.37 ^a
NaBr ^{e,p}	0.50	0.73	0.49	-0.19	-1.46	-3.91 ^a
NaI ^{e,p}	0.53	0.75	0.18	-0.91	-2.89	-5.27 ^a
-298 $\Delta S_{tr}^{\circ}/\text{kcal mol}^{-1}$ (molar scale) ^b						
LiCl ^e	0.03	0.23	1.12	2.59	4.90	7.2 ^d
NaCl ^e	0.00	0.14	1.01	2.41	4.70	8.0 ^d
KCl ^e	0.04	0.29	1.28	2.69	4.84	8.1 ^d
RbCl ^e	0.04	0.30	1.33	2.74	4.69	7.5 ^d
CsCl ^e	0.01	0.26	1.35	2.79	4.53	7.1 ^d
NaBr ^e	-0.12	0.04	1.06	2.63	4.97	8.5 ^d
NaI ^e	-0.22	-0.12	0.98	2.77	5.59	9.0 ^d

(a) Idealised volume fraction of methanol; (b) 1 cal = 4.184 J; (c) ± 50 cal mol⁻¹ or better; (d) ± 100 cal mol⁻¹; (e) ± 200 cal mol⁻¹; (f) ref. 22(a) (g) ref. 23; (h) D. Feakins, K. G. Lawrence, and P. J. Voice, *J. Chem. Soc. (A)*, 1970, 837; (i) interpolated from original data; (j) ref. 14(a); (k) ref. 1 (l) ref. 22(b); (m) ref. 14(b); (n) ref. 14(c); (o) ref. 15; (p) ref. 40; (q) Table 2.

Table 6 Standard free energies (ΔG_{tr}°), enthalpies (ΔH_{tr}°), and entropies (ΔS_{tr}°) of transfer of electrolytes from water to mixtures of water and dimethyl sulphoxide at 25°C

Salt	ϕ_{DMSO}^e	Wt % DMSO	$\Delta G_{tr}^\circ/\text{kcal mol}^{-1}$ (molar scale) ^b					0.90	1.00
			0.10	0.20	0.40	0.60	0.70		
LiCl ^{c,f}	0.15 ^g	0.29 ^g	0.68 ^g	1.20 ^h	1.60 ^h	2.04 ^h	3.08 ^h	5.6 ^{d,i}	
NaCl ^{c,f}	0.21 ^g	0.51 ^g	1.28 ^g	2.31 ^h	2.92 ^h	3.52 ^h	4.56 ^h	6.1 ^{d,i,j}	
KCl ^{c,f}	0.24 ^g	0.53 ^g	1.36 ^g	2.68 ^h	3.35 ^h	4.09 ^h	5.00 ^h	6.3 ^{d,k}	
RbCl ^{c,f}	0.24 ^g	0.52	1.32	2.53 ^h	3.45 ^h	4.15 ^h	5.21 ^h	6.6 ^{d,k}	
CsCl ^{c,f}	0.22 ^g	0.50 ^g	1.30 ^g	2.30 ^h	2.94 ^h	3.60 ^h	4.51 ^h	6.2 ^{d,k}	
AgCl ^{e,f}	0.04 ^g	0.08 ^g	0.16 ^g	0.10 ^{c,g}	0.1 ^{d,l}	0.2 ^{d,l}	0.6 ^{d,l}	1.4 ^{d,k}	
KBr ^{c,m}	0.11	0.31	0.82	1.48	1.75	2.00	2.33	2.8 ^{d,n}	
KI ^{c,m}	0.02 ^g	0.06	0.12	0.18	0.21	0.24	0.27	0.3 ^{d,k}	
Ph ₄ AsI ^{c,m}	-0.41	-0.90	-1.99	-3.05	-3.50	-4.10	-4.79	-5.60 ^{d,k}	
KBPh ₄ ^{c,m}	-0.50	-1.09	-2.60	-4.80	-6.22	-7.81	-9.63	-11.7 ^{d,k}	
				$\Delta H_{tr}^\circ/\text{kcal mol}^{-1b}$					
LiCl ^{e,m}	-0.5	-1.0	-0.2	-0.7	-0.8	-1.4	-1.8	-2.1 ^o	
NaCl ^{d,m}	-0.1	-0.2	-0.7	-0.8	-2.0	-2.6 ^p	-3.0	-4.3 ^p	
KCl ^{d,m}	-0.1	-0.4	-0.7	-1.9	-2.0	-4.3 ^p	-4.9 ^p	-3.8 ^p	
RbCl ^{d,m}	-0.1	-0.1	-0.4	-1.1	-4.2	-7.8 ^q	-10.0	-7.8 ^q	
CsCl ^{d,m}	-0.5	-2.0	-3.4	-4.2	11.7	10.0	11.7	10.0	
AgCl ^{e,m}	3.0	10.4	10.4	11.0	-4.2	-5.6	-7.5 ^p	-7.5 ^p	
n-Bu ₄ NCl ^{e,r}	-0.4	-0.8	-1.7	-3.2	-4.2	-5.6	-7.5 ^p	-7.5 ^p	
KBr ^{d,m}	-0.4	-0.8	-1.7	-3.2	-4.2	-5.6	-7.5 ^p	-7.5 ^p	

	-0.8	-1.6	-3.2	-6.9	-11.3 ^p
KI ^{d,m}					
n-Bu ₄ NI ^{e,r}		7.6	7.9	7.2	3.3
NaBPh ₄ ^{e,r}	3.5 ^f	0.3	-3.0	-6.3	-9.8
		-298 ΔS _{tr} ^o /kcal mol ⁻¹ (molar scale) ^b			
LiCl ^e	0.8	1.7	2.3 ^f	2.9 ^f	3.4
NaCl ^e	0.6	1.4 ^f	2.5	3.6	4.3
KCl ^e				4.2	6.1
RbCl ^e	0.6	1.7	3.2	5.4	
CsCl ^e	0.6	1.4	2.7	4.0	11.5
AgCl ^e	0.6	2.2	3.5	4.3	10.0
KBr ^e	0.7	1.6	3.2	5.0	9.2
KI ^e	0.9		1.8	3.4	11.6
				4.9	7.7
				8.0	8.7
					10.6
					11.5
					10.0
					9.2
					10.3
					7.2

(a) Idealised volume fraction of dimethyl sulphoxide; (b) 1 cal = 4.184 J; (c) ±50 cal mol⁻¹ or better; (d) ±100 cal mol⁻¹; (e) ±500 cal mol⁻¹; (f) interpolated value; (g) ref. 31; (h) ref. 24(c); (i) ref. 19(b); (j) ref. 9; (k) B. G. Cox, *Ann. Rep. Chem. Soc. (A)*, 1973, 249; (l) J. P. Morel, *Bull. Soc. Chim. Fr.*, 1968, 896; (m) ref. 16(b); (n) ref. 8; (o) R. Fuchs, J. C. Bear, and R. F. Rodewald, *J. Amer. Chem. Soc.*, 1969, 91, 5797; (p) from data in ref. 9; (q) ref. 44; (r) ref. 35.

Table 7 Standard free energies (ΔG°_{tr}), enthalpies (ΔH°_{tr}), and entropies (ΔS°_{tr}) of transfer of electrolytes from propylene carbonate to mixtures of propylene carbonate and dimethyl sulphoxide at 25°C

ϕ_{DMSO}^a	0.0	0.01	0.02	0.05	0.10	0.20	0.40	1.00		
Wt % DMSO	0.0	0.085	1.7	4.3	8.6	17.5	36.2	100		
Salt	$\Delta G^\circ_{tr}/\text{kcal mol}^{-1}$ (molar scale) ^b									
AgCl ^{c,e}	0.0	-3.0	-3.9	-5.6	-7.1	-8.7	-10.3	-12.8		
AgBr ^{c,e}	0.0	-1.6	-2.0	-4.1	-5.5	-6.8	-8.3	-10.8		
NaCl ^{c,f}	0.0	-0.6	-0.8	-1.7	-2.7	-3.8	-5.2	-7.2		
		$\Delta H^\circ_{tr}/\text{kcal mol}^{-1b}$								
AgCl ^{c,e}	0.0	-7.0	-8.9	-10.9	-12.3	-12.5	-12.9	-14.0		
AgBr ^{c,e}	0.0	-7.5	-9.4	-10.5	-11.9	-12.9	-13.4	-14.4		
AgI ^{c,e}	0.0	-7.5	-9.2	-10.9	-11.9	-12.7	-13.8	-14.5		
AgClO ₄ ^{c,h}	0.0	-8.1	-9.6	-10.7	-11.8	-11.4	-11.7	-12.2		
LiClO ₄ ^{c,h}	0.0	-5.2	-6.2	-7.5	-8.3	-8.4	-8.8	-8.8		
NaClO ₄ ^{c,h}	0.0	-1.6	-2.0	-3.4	-3.9	-4.2	-4.8	-5.0		
NaBPh ₄ ^{c,h}	0.0	-0.5	-1.2	-2.5	-3.7	-4.3	-4.6	-3.5 ^f		
Ph ₄ AsClO ₄ ^{c,h}	0.0	0.0	0.0	-0.3	-0.5	-0.5	-0.5	-0.6 ^a		
		$-298 \Delta S^\circ_{tr}/\text{kcal mol}^{-1}$ (molar scale) ^b								
AgCl	0.0	4.0	5.0	5.3	5.2	3.8	2.6	1.2		
LiCl	0.0	2.5	4.5	3.5	3.3	2.7	1.3	-0.2		
NaCl	0.0	0.2	0.5	1.9	1.7	1.5	0.8	-0.4		

(a) Idealised volume fraction of dimethyl sulphoxide; (b) 1 cal = 4.184 J; (c) ± 200 cal mol⁻¹; (d) ± 500 cal mol⁻¹; (e) B. G. Cox, T. Clune, and W. E. Waghorne, unpublished results; (f) calculated from ref. 25 and 26; (g) calculated from ref. 25 and 50; (h) ref. 26; (i) C. V. Krishnan and M. L. Friedman, *J. Phys. Chem.*, 1969, 73, 3984.

5, and 6 list values of $\Delta G^\circ_{\text{tr}}$, $\Delta H^\circ_{\text{tr}}$, and $-298 \Delta S^\circ_{\text{tr}}$ from water into the binary solvent systems $\text{H}_2\text{O} + \text{CH}_3\text{CN}$, $\text{H}_2\text{O} + \text{CH}_3\text{OH}$, and $\text{H}_2\text{O} + \text{dimethyl sulphoxide (DMSO)}$, and Table 7 lists values of $\Delta G^\circ_{\text{tr}}$, $\Delta H^\circ_{\text{tr}}$, and $-298 \Delta S^\circ_{\text{tr}}$ from propylene carbonate (PC) to $\text{PC} + \text{DMSO}$ solvent systems. The ΔS° values are reported as $-298 \Delta S^\circ$ to facilitate comparisons with the ΔG° and ΔH° data, which are reported at 298 K.

The data listed in Tables 1 to 7 are the most reliable available in each case; where no single set of data appears to be superior to others the values reported are averages of the reliable data. The precisions listed for the experimental data were assessed from comparisons with other available data and from the additivity of the data. They generally correspond to those estimated by the original authors. The solvent compositions for which data are listed in each of the mixed solvent systems are those predominantly used by the original authors, to minimize the number of interpolations required.

The free energy data were obtained from solubilities,⁸⁻¹⁶ corrected to infinite dilution *via* the Davies equation¹⁷ where necessary; from e.m.f. measurements of reversible electrochemical cells;¹⁸⁻²⁶ or from measurements of polarographic half-wave²⁷⁻³⁰ potentials. This last method yields only approximate values because of the dependence of the half-wave potential on the diffusion coefficients of the reactant and product, as well as on the activities of the electroactive

⁸ R. Alexander, A. J. Parker, J. H. Sharp, and W. E. Waghorne, *J. Amer. Chem. Soc.*, 1972, **95**, 1148.

⁹ I. M. Kolthoff and M. K. Chantooni, *J. Phys. Chem.*, 1972, **76**, 2024.

¹⁰ M. H. Abraham, *J.C.S. Faraday I*, 1973, **69**, 1375.

¹¹ P. J. M. Brocca, R. Phillips, S. J. Goldberg, and O. Popovych, *J. Chem. Eng. Data*, 1979, **24**, 215.

¹² D. R. Cogley, J. N. Butler, and E. Grunwald, *J. Phys. Chem.*, 1971, **75**, 1477.

¹³ J. Courtôt-Coupez and M. L'Her, *Bull. Soc. Chim. Fr.*, 1969, 675.

¹⁴ K. P. Anderson, E. A. Butler, and E. M. Woolley, *J. Phys. Chem.*, (a) 1971, **75**, 93; (b) 1973, **77**, 2564; (c) 1974, **78**, 2244.

¹⁵ C. L. de Ligny, D. Bax, M. Alfenaar, and M. G. L. Elferink, *Rec. Trav. Chim.*, 1969, **88**, 1183.

¹⁶ B. G. Cox, R. Natarajan and W. E. Waghorne, *J.C.S. Faraday I*, 1979, **75**; (a) p. 86; (b) p. 1780.

¹⁷ C. W. Davies, 'Ion Association', Butterworth, London, 1962, eqn. 3.14.

¹⁸ B. Scrosati, S. Shiuvo, and G. Pecci, *Ric. Sci.*, 1968, **38**, 367.

¹⁹ M. Salomon, (a) *J. Electroanal. Chem.*, 1970, **26**, 319; (b) *J. Electrochem Soc.*, 1970, **117**, 325.

²⁰ J. N. Butler and J. C. Synnott, (a) *J. Amer. Chem. Soc.*, 1970, **92**, 2602; (b) *Anal. Chem.*, 1969, **41**, 1890.

²¹ W. H. Symral and C. W. Tobias, *J. Electrochem Soc.*, 1968, **115**, 33.

²² D. Feakins and P. J. Voice, *J.C.S. Faraday I*, (a) 1972, **68**, 1390; (b) 1973, **69**, 1711.

²³ A. K. Covington and J. M. Thain, *J.C.S. Faraday I*, 1975, **71**, 78.

²⁴ R. Smits, D. L. Massart, J. Jouillard, and J. P. Morel, *Electrochim Acta*, 1976, **21**, (a) p. 425; (b) p. 431; (c) p. 437.

²⁵ B. G. Cox, A. J. Parker, and W. E. Waghorne, *J. Phys. Chem.*, 1974, **78**, 1731.

²⁶ B. G. Cox, W. E. Waghorne, and C. K. Pigott, *J.C.S. Faraday I*, 1979, **75**, 227.

²⁷ J. Courtôt-Coupez, M. Le Démézet, A. Laouenen, and C. Madec, *J. Electroanal. Chem.*, 1971, **29**, 21.

²⁸ M. L'Her, D. Morin-Bozec, and J. Courtôt-Coupez, *J. Electroanal. Chem.*, 1974, **55**, 133.

²⁹ G. Gritzner, *Inorg. Chim. Acta*, 1977, **24**, 5.

³⁰ J. Massaux and G. Duyckaerts, (a) *J. Electroanal. Chem.*, 1975, **59**, 311; (b) *Bull. Soc. Chim. Belg.*, 1975, **84**, 519.

species in solution. However, where polarographic data could be compared with solubility or e.m.f. data in the solvents of interest, agreement was acceptable for reversible systems.

The e.m.f. measurements in aprotic solvent systems are difficult because of the lack of anion-sensitive electrodes suitable for these media. The use of silver/silver halide electrodes is complicated by the formation of anionic silver halide complexes^{16,31} $[\text{AgX}_n]^{(n-1)-}$ and the scatter in data obtained using the analogous thallium amalgam/thallic halide electrodes^{19-21,27,32} indicates that similar difficulties may be associated with their use.

Enthalpy data were obtained from direct calorimetric measurements of the heats of solution^{16,33-37} or precipitation of electrolytes,^{16,38,39} or of heats of dilution of electrolyte solutions into appropriate solvent mixtures,^{26,40} or indirectly from the temperature dependence^{19,20} of the e.m.f.'s of electrochemical cells.

A comprehensive compilation of enthalpy data for electrolytes and non-electrolytes in single-component solvent systems has recently been published⁴¹ and only a part of those data, together with some more recent results, is listed here.

Entropy data were obtained from the free energy and enthalpy data *via* equation (1):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (1)$$

Correspondingly the entropy data are less precise, since they contain the experimental errors of both the free energy and enthalpy values.

A number of general observations about the data in Tables 1 to 7 may be usefully made at this point without anticipating the more detailed considerations of ionic solvation which appear later.

A. Free Energy Data.—The free energy data are, perhaps, more easily visualised in terms of the solubilities of the electrolytes in the various solvents. The solubility product of an electrolyte in solvent S, $K_{\text{sp}}(\text{S})$, is related to its free energy of solution in solvent S, $\Delta G^\circ_{\text{s}}(\text{S})$, by equation (2). It then follows directly from equations (3) and (4) that, for a given electrolyte, the more favourable the $\Delta G^\circ_{\text{tr}}$ value, the more soluble is the electrolyte in solvent S. Absolute values of the solubility products in the various solvent systems may be obtained by the application of equations (2) and (3) to the data in Tables 1 and 4-7.

³¹ D. Feakins, B. E. Hickey, and P. J. Voice, *J.C.S. Faraday I*, 1979, **75**, 907.

³² N. Matsuura and K. Umemoto, *Bull. Chem. Soc. Japan*, 1974, **47**, 1334.

³³ C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, 1971, **75**, 3606.

³⁴ L. Weeda and G. Somsen, *Rec. Trav. Chim.*, 1967, **86**, 893.

³⁵ R. Fuchs and C. P. Hagen, *J. Phys. Chem.*, 1973, **77**, 1797.

³⁶ E. M. Arnett and D. R. McKelvey, *J. Amer. Chem. Soc.*, 1966, **88**, 2598.

³⁷ M. E. Estep, D. D. Macdonald, and J. B. Hyne, *J. Solution Chem.*, 1977, **6**, 129.

³⁸ Y. C. Wu and H. L. Friedman, *J. Phys. Chem.*, 1966, **70**, 501.

³⁹ B. G. Cox and A. J. Parker, *J. Amer. Chem. Soc.*, 1973, **95**, 402.

⁴⁰ E. de Valera, D. Feakins, and W. E. Waghorne, *J.C.S. Faraday I*, 1980, **76**, 560.

⁴¹ C. V. Krishnan and H. L. Friedman, 'Solute-Solvent Interactions', ed. J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York, 1976.

$$\Delta G^{\circ}_s(S) = -RT \ln K_{sp}(S) \quad (2)$$

$$\Delta G^{\circ}_{tr}(H_2O \rightarrow S) = \Delta G^{\circ}_s(S) - \Delta G^{\circ}_s(H_2O) \quad (3)$$

$$= -RT \ln [K_{sp}(S)/K_{sp}(H_2O)] \quad (4)$$

The results in Tables 1 and 4—7 show that simple inorganic salts are generally more soluble in water than in any of the non-aqueous or mixed aqueous solvent systems [*i.e.* $\Delta G_{tr}(H_2O \rightarrow S) > 0$]. The exceptions are some iodide salts in formamide, AgBr and AgI in formamide and DMSO, and silver halides and CuCl in aqueous acetonitrile solvent systems. The solubilities of inorganic electrolytes, other than silver and cuprous salts, generally decrease in the order $H_2O > \text{formamide} > \text{DMSO} > \text{MeOH} > \text{DMF} > \text{PC} > \text{MeCN}$. Of the other commonly studied solvents, the solubilities in *N*-methylformamide^{42,43} are similar to those in formamide; sulpholane⁴⁴ and acetone⁸ are similar to PC; and *N*-methyl-2-pyrrolidone (NMePy),^{44,45} hexamethylphosphoramide (HMPA),⁸ dimethylacetamide,⁸ and ethanol are comparable to DMSO, MeOH, and DMF.

In the binary solvent systems, the solubilities of simple inorganic electrolytes all vary monotonically, or occasionally pass through maxima (minima in ΔG°_s), but do not show minima.

The variations in electrolyte solubilities show no correlation with the simple physical properties of the solvent systems, such as their dielectric constants or dipole moments; for example, PC has a higher dielectric constant (65) and dipole moment (4.94 D) than MeOH (32.6 and 1.70 respectively), yet electrolytes are considerably more soluble in the latter. It is true that electrolytes are significantly less soluble in dichloroethane,⁴⁶ which has an extremely low dielectric constant (10.2), but this probably reflects an underlying factor rather than a direct causal relationship.

There are, however, obvious trends in the ΔG°_{tr} data for inorganic electrolytes which can be rationalized in terms of the nature of the solvents. Variations in anionic solvation are reflected in the ΔG°_{tr} data for any series of electrolytes MX having a common cation M. These ΔG°_{tr} values become increasingly unfavourable in the order $\text{ClO}_4^- < \text{I}^- < \text{Br}^- < \text{Cl}^-$ on transfer from protic solvents (H_2O , MeOH, formamide), which can interact with anions *via* their acidic protons, to aprotic solvents (DMF, DMSO, PC, MeCN *etc.*), which do not have such well-defined centres of positive charge. The order reflects the charge density of the anion, the interactions being stronger for (small) anions with high charge density. This difference between the behaviour of anions of high and low charge density accounts for the large rate increases observed for organic reactions involving anionic bases and nucleophiles as reactants on transfer from protic to aprotic solvents,⁴⁷ and also for the increased stabilities of halide complexes such as ZnCl_4^{2-} in aprotic solvents relative to those in protic solvents.⁴⁸

⁴² C. L. de Ligny, H. J. M. Denessen, and M. Alfenaar, *Rec. Trav. Chim.*, 1971, **90**, 1265.

⁴³ E. Luksha and C. M. Criss, *J. Phys. Chem.*, 1966, **70**, 1496.

⁴⁴ B. G. Cox, G. R. Hedwig, A. J. Parker, and D. W. Watts, *Aust. J. Chem.*, 1974, **27**, 477.

⁴⁵ P. O. I. Virtanen and R. Kerkela, *Suomen. Kem.*, 1969, **42**, 29.

⁴⁶ M. H. Abraham and A. F. Danil de Namor, *J.C.S. Faraday I*, 1976, **72**, 955.

⁴⁷ A. J. Parker, *Chem. Rev.*, 1969, **69**, 1.

⁴⁸ S. Ahrland and N. O. Bjork, *Coord. Chem. Rev.*, 1975, **16**, 115.

The $\Delta G^\circ_{\text{tr}}$ values for the series of alkali-metal halides having a common anion X are increasingly favourable (or less unfavourable) in the order Cs \sim Rb < K < Na < Li for transfer from water to solvents which are better Lewis bases (e.g. H₂O \rightarrow DMSO, DMF, HMPA,⁸ NMePy^{44,45}); and *vice versa* for transfer to solvents which are poorer Lewis bases (e.g. PC, MeCN, sulpholane⁴⁴). This order is also observed for transfer between non-aqueous solvents on transfer from a poorer to a better solvent in terms of Lewis basicity, reflecting the relatively greater importance of such interactions for the smaller cations. These trends with solvent basicity may be considered more quantitatively in terms of Gutmann's donor numbers,⁴⁹ which are a measure of the electron-donating ability of the solvents.

Clearly ion-solvent interactions other than these simple acid-base/electrostatic interactions are possible.^{31,50} For example, the differences between the behaviour of $\Delta G^\circ_{\text{tr}}$ for Cu⁺ and Ag⁺ compared with alkali-metal salts on transfer from water to acetonitrile/water systems reflect the strong interaction of these univalent d^{10} cations with the nitrilic solvent;^{8,16a} the results are not unexpected in view of the strength of the Cu⁺ and Ag⁺-MeCN complexes in water.⁵¹ More remarkable results were obtained for solvents such as dimethylthioformamide (DMTF)^{50,52} where, for example, AgI is much more soluble than KI.

Data for multiply charged ions are more limited. They generally reflect the trends observed for univalent ions, but with much larger variations,⁵³ as might be expected from their larger charge densities (e.g. Fe²⁺, Fe³⁺, Cu²⁺ salts in MeCN + H₂O, Table 4).

For the tetra-alkylammonium salts (R₄N⁺ X⁻), $\Delta G^\circ_{\text{tr}}$ values become increasingly more negative with increasing size of R, for transfer from water to all other solvents. The solubilities of these salts, and others containing similarly large organic ions, are also generally greater in non-aqueous and mixed aqueous solvents, in marked contrast to those of the simple inorganic electrolytes. The variations in $\Delta G^\circ_{\text{tr}}$ of electrolytes containing such ions are similar to those of non-electrolytes, and are the result of 'hydrophobic' interactions. These have recently been discussed elsewhere,⁵⁴ and will not be considered in detail here.

B. Enthalpies and Entropies of Transfer.—A number of interesting features are immediately apparent from these data (Tables 2—7). Perhaps the most striking is that the $\Delta H^\circ_{\text{tr}}$ values from water are favourable ($\Delta H^\circ_{\text{tr}} < 0$) for simple electrolytes in almost all cases except for MeOH + H₂O mixtures, despite the fact that the corresponding $\Delta G^\circ_{\text{tr}}$ values are predominantly unfavourable. Nevertheless

⁴⁹ V. Gutmann, 'Coordination Chemistry in Non-aqueous Solutions', Springer-Verlag, Vienna, 1968.

⁵⁰ R. Alexander, D. A. Owensby, A. J. Parker, and W. E. Waghorne, *Aust. J. Chem.*, 1974, **27**, 933.

⁵¹ S. E. Manahan and R. J. Iwamoto, *J. Electroanal. Chem.*, 1967, **14**, 213.

⁵² J. G. Clune, W. E. Waghorne, and B. G. Cox, *J.C.S. Faraday I*, 1976, **27**, 1294.

⁵³ G. R. Hedwig, D. A. Owensby, and A. J. Parker, *J. Amer. Chem. Soc.*, 1975, **97**, 3888.

⁵⁴ A. Ben Naim, 'Hydrophobic Interactions', Plenum Press, London, 1980.

many of the trends considered above for the $\Delta G^\circ_{\text{tr}}$ values also apply to the $\Delta H^\circ_{\text{tr}}$ values. For example, $\Delta H^\circ_{\text{tr}}$ values for a series of electrolytes MX having a common cation become increasingly unfavourable in the order $\text{I}^- < \text{Br}^- < \text{Cl}^-$ for transfer from protic to aprotic solvents, as do the $\Delta G^\circ_{\text{tr}}$ values.

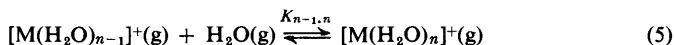
A second interesting feature is that $\Delta S^\circ_{\text{tr}}$ values of simple electrolytes between single-component solvent systems are relatively independent of the electrolyte, but strongly dependent on the solvent. For example, the $-298\Delta S^\circ_{\text{tr}}$ values of simple electrolytes from H_2O to MeCN are $12.5 \pm 0.5 \text{ kcal mol}^{-1}$ excepting LiCl (data from Table 3). Thus it appears that these $\Delta S^\circ_{\text{tr}}$ values predominantly reflect changes in the properties of the solvent systems (*cf.* below).

It is also clear from the data in the binary solvent systems that the variations in $\Delta H^\circ_{\text{tr}}$ and $\Delta S^\circ_{\text{tr}}$ with changing solvent composition are more complex than those for $\Delta G^\circ_{\text{tr}}$.

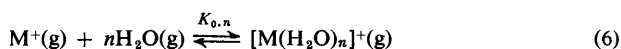
As with the $\Delta G^\circ_{\text{tr}}$ values, the $\Delta H^\circ_{\text{tr}}$ and $\Delta S^\circ_{\text{tr}}$ values of electrolytes having large organic ions more closely resemble the values for non-electrolytes than those of the simple inorganic electrolytes.⁵⁴

3 Ion-Solvent Interactions in the Gas Phase

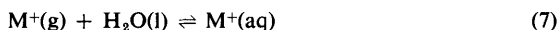
A recent development in the study of ion-solvent interactions has been the investigation of equilibria between ions and solvent molecules in the gas phase, by use of mass spectrometric techniques.⁵⁵⁻⁵⁸ The equilibrium constants for the addition of successive solvent molecules to ions in the gas phase are measured directly [*e.g.* equation (5) for water molecules]. Wide ranges of temperature



(normally several hundred °C) are necessary to bring the different equilibria into an accessible region, but by extrapolation it is possible to obtain the successive equilibrium constants, or equilibrium products [equation (6)], at a constant temperature (298 K).



An obvious area of interest in these results is the relationship between the energies involved in equilibria (5) and (6) and the total solvation energies of the ions [equation (7) for cations and similarly for anions]. In order to facilitate



comparison between gas-phase equilibrium data and hydration energies, the standard state for water of 1 atmosphere at 298 K used in the original publications^{56,57,59} has been converted to that of pure water, corresponding to equation

⁵⁵ S. K. Searles and P. Kebarle, *Can. J. Chem.*, 1969, 47, 2619.

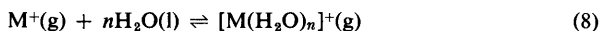
⁵⁶ M. Arshadi, R. Yamdagni, and P. Kebarle, *J. Phys. Chem.*, 1970, 74, 1475.

⁵⁷ W. R. Davidson and P. Kebarle, *J. Amer. Chem. Soc.*, 1976, 98, 6125.

⁵⁸ R. C. Burnier, T. J. Culin, W. D. Reents, R. B. Cody, R. K. Lengel, and B. S. Freiser, *J. Amer. Chem. Soc.*, 1979, 101, 7127.

⁵⁹ I. Dzidic and P. Kebarle, *J. Phys. Chem.*, 1970, 74, 1466.

(8). Results for alkali-metal cations and halide anions with water as solvent are given in Table 8.



Considering first the cations, it may be seen that there is a steady decrease in the free energy of complex formation with the addition of successive water molecules (*i.e.* ΔG becomes less negative); the values have become very small by the time 5–6 water molecules have been added. Beyond this point the decrease in free energy on complex formation is only very slightly greater than the free energy of condensation of a water molecule from the gas phase to liquid water. Despite this, however, the total interaction energy is still very much lower than the hydration energies; the remainder of the hydration energy must come from the summation of a very large number of small terms. An important point, though, is that the *difference* between the energy liberated on addition of 5–6 water molecules and the total hydration energy is almost independent of the cation (61 ± 4 kcal mol⁻¹). This suggests that, at least for the alkali-metal cations, differences in hydration energies result primarily from differences in interactions within the first 1–2 layers of solvent molecules, and that specific size-dependent interactions are not transmitted through a number of layers.

The same general pattern obtains for the halide ions, although, except for F⁻, $\Delta G^{\circ}_{0,n}$ values tend to level off after the addition of a smaller number of water molecules (3–4). The difference between the ‘first-sphere’ values and the total solvation energies of the anions is again almost constant (50 ± 5 kcal mol⁻¹).

Kebarle and co-workers have also determined equilibrium constants for the interaction of anions and cations with acetonitrile in the gas phase.^{57,60} Results for K⁺ and Cl⁻ are compared with corresponding values for interaction with water in Table 9. In view of the fact that all of the simple alkali-metal halide salts are more soluble in water, and acetonitrile + water mixtures, than in acetonitrile (Tables 1 and 4), it is striking that both K⁺ and Cl⁻ (and indeed all other alkali-metal cations and halide ions, except F⁻)^{57,60} interact more strongly with acetonitrile than with water in the gas phase. The difference is most marked for the addition of the first two solvent molecules, and it appears that, beyond $n = 4$, the further addition of solvent molecules tends to reduce the difference in the total interaction energies.

A possible explanation⁶¹ for this apparent contradiction is that the superior solvating ability of water comes predominantly from co-operative effects in bulk water (*i.e.* solvation effects passed through H-bonds). However, although such effects probably account for the more gradual fall-off in the interaction energies of successive water molecules compared with the sharp drop observed after the addition of the first four acetonitrile molecules (Tables 8, 9), they cannot completely resolve the problem. Thus it is clear from the results in acetonitrile + water mixtures (Table 4), and from the detailed work of Chantooni and Kolthoff⁶²

⁶⁰ R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, 1972, **94**, 2940.

⁶¹ E. M. Arnett, B. Chawla, and N. J. Hornung, *J. Solution Chem.*, 1977, **6**, 781.

⁶² M. K. Chantooni and J. M. Kolthoff, *J. Amer. Chem. Soc.*, 1967, **89**, 1582.

Table 8 Interaction between ions and water molecules in the gas phase at 298 K^a

$$M^+(g), X^-(g) + nH_2O(l) \xrightarrow{\Delta G_{0,n}} [M(H_2O)_n]^+(g), [X(H_2O)_n]^-(g)$$

$\Delta G_{0,n}$ /kcal mol ^{-1b}	M ⁺						X ⁻			
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺		F ⁻	Cl ⁻	Br ⁻	I ⁻
- $\Delta G_{0,1}$	23.4	15.5	9.3	7.5	5.8		16.0	6.1	4.9	3.3
- $\Delta G_{0,2}$	40.2	26.6	15.9	12.4	9.6		24.9	10.5	8.3	5.4
- $\Delta G_{0,3}$	51.4	33.8	20.1	15.3	11.7		30.4	12.8	10.3	6.4
- $\Delta G_{0,4}$	56.8	38.0	22.4	17.0	12.6		34.9	14.0	11.1	6.6
- $\Delta G_{0,5}$	59.2	39.8	23.5	17.7	13.0		37.9	14.8	11.5	
- $\Delta G_{0,6}$	59.6	40.6	23.7	18.0						
- $\Delta G_{0,n}^{c,d}$	125.6	101.8	84.1	79.0	71.3		83.4	70.0	63.1	54.2

(a) Values from ref. 56 and 59 corrected to a standard state for water of liquid water at 298 K; (b) 1 cal = 4.184 J; (c) Free energies of hydration; (d) ref. 78.

Table 9 Complex formation of K⁺, Cl⁻ with H₂O and CH₃CN molecules in the gas phase at 298 K^a

$$[I(S)_{n-1}]^-(g) + S(l) \xrightleftharpoons{\Delta G_{n-1,n}} [I(S)_n]^-(g)$$

$\Delta G_{n-1,n}$ /kcal mol ^{-1b}	I = K ⁺			I = Cl ⁻		
	S = H ₂ O	S = CH ₃ CN		S = H ₂ O	S = CH ₃ CN	
- $\Delta G_{0,1}$	9.3	16.8		6.1	8.0	
- $\Delta G_{1,2}$	6.6	12.2		4.4	5.4	
- $\Delta G_{2,3}$	4.2	8.6		2.3	3.4	
- $\Delta G_{3,4}$	2.3	4.2		1.2	1.8	
- $\Delta G_{4,5}$	1.1	0.2		0.8	—	

(a) Values from refs 56, 57, 59, 60 corrected to standard states for water and acetonitrile of the pure liquid at 298 K; (b) 1 cal = 4.184 J.

and Benoit and Lam⁶³ using very dilute solutions of water in acetonitrile, that, in the liquid phase, water molecules interact more strongly than acetonitrile with electrolytes such as KCl, whether in pure water, acetonitrile + water mixtures, or very dilute solutions of water in acetonitrile. Similar results have also been found for water in other poorly solvating media such as propylene carbonate¹² and sulpholane.⁶³

An alternative explanation for the observed difference between the results for ion-solvent interactions involving water and acetonitrile molecules in the gas and liquid phase might be that polarisability effects are much more important in the gas phase. Thus an acetonitrile molecule is significantly larger and more polarisable than a water molecule, and hence better able to stabilise a charge in the gas phase. In solution, where charges may be stabilised by interaction over a large number of solvent molecules, the relative polarisabilities of different solvent molecules in the immediate neighbourhood of ions may not be as important. Polarisability effects have been shown to be particularly important in the gas phase for the stabilisation by alkyl groups of both positive and negative charges resulting from gain or loss of protons by alkylamines.⁶⁴

Thus, it seems that gas-phase studies of ion-solvent interactions may provide much information of interest and relevance to ion solvation, but it is not yet clear the extent to which differences between ion-solvent interactions for various solvent molecules in the gas phase can be related to corresponding differences in ion solvation in the liquid phase. Further studies on a wider range of solvent molecules should help to clarify this point.

The use of analogous stability constant data for ion-solvent interactions obtained in solution to interpret free energies of transfer of ions between solvents is discussed below.

4 Theoretical Studies of Ion-Solvent Interactions

The thermodynamic parameters for transfer of electrolytes among solvents are experimental quantities, and as such do not constitute an explanation of solvation phenomena. In order to understand the variations in these parameters it is necessary to develop a satisfactory model to represent the ion-solvent system.

The simplest of these involves the representation of the solvent as a continuum.⁶⁵ The properties of the solvent are assumed to be unaffected by the presence of the ion, and the molecularity of the solvent is ignored. This model has been used successfully to account for a number of solution phenomena, most notably ion-ion interactions *via* the Debye-Hückel theory.⁶⁶ However, in dealing with ionic solvation, a more realistic model is needed. For example, a continuum model can only account for electrostatic interactions, with the solvent contribution arising *via* its bulk dielectric constant. As was pointed out above, ΔG°_{tr}

⁶³ R. L. Benoit and S. Y. Lam, *J. Amer. Chem. Soc.*, 1974, **96**, 7835.

⁶⁴ J. I. Braumann and L. K. Blair, *J. Amer. Chem. Soc.*, 1971, **93**, 3911.

⁶⁵ M. Born, *Z. Physik.*, 1920, **1**, 45.

⁶⁶ R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions', Butterworths, London, 1965, 2nd edn.

values for electrolytes do not correlate with solvent dielectric constants. Moreover, it is clear from the earlier qualitative discussion of the results that the molecularity of the solvent, at least in the immediate vicinity of the ion, must be taken into account in any successful solvation model.

Bernal and Fowler⁶⁷ proposed a more satisfactory model for the solvent around the ion, whereby the solvent is represented by three concentric shells. The inner, or co-ordination shell, contains those solvent molecules in intimate contact with the ion, the intermediate shell the remaining solvent affected by the presence of the ions, and the outer shell the unaffected bulk solvent. This model has been used successfully to explain qualitatively the variations in data such as the entropies of hydration^{68,69} and transfer⁴⁴ of electrolytes *via* Frank and Evans⁶⁸ analysis of the creation and disruption of solvent structure.

Quantitative treatment of solvation data based on this model involves assessment of the interaction of the ion with each of the shells of solvent molecules. The interaction of an ion with the outer shell of solvent molecules can be calculated by treating the bulk solvent as a continuum and using the Born equation.⁶⁵ The neglect of solvent molecularity is reasonable, as the radius of the intermediate shell is much greater than those of individual solvent molecules. However, although these calculations are simple, the outer-shell interactions make only a small contribution to the thermodynamic parameters for transfer of electrolytes among common solvents. For example, for transfer of NaCl from PC ($\epsilon = 64.7$) to MeOH ($\epsilon = 32.6$), interactions beyond two molecular diameters would contribute only $+0.6 \text{ kcal mol}^{-1}$ to $\Delta G^{\circ}_{\text{tr}}$, whereas the overall change is $-7.6 \text{ kcal mol}^{-1}$. Thus, it is clear that an accurate assessment of the interaction of an ion with those solvent molecules in its immediate vicinity is central to a quantitative treatment of ionic solvation.

A number of approaches have been used to calculate the ion-solvent interaction energies involving solvent molecules close to the ion, but most have been based on a simplified two-state model in which the intermediate shell is treated as part of the bulk solvent. One such approach has been to treat the solvent in the co-ordination shell as a continuum, but with a dielectric constant lower than that of the bulk solvent.⁷⁰⁻⁸² The reduced dielectric constant reflects the restricted

⁶⁷ J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, 1933, **1**, 515.

⁶⁸ H. S. Frank and M. W. Evans, *J. Chem. Phys.*, 1945, **13**, 507.

⁶⁹ H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, 1957, **24**, 133.

⁷⁰ T. J. Webb, *J. Amer. Chem. Soc.*, 1926, **48**, 2589.

⁷¹ C. K. Ingold, *J. Chem. Soc.*, 1931, 2179.

⁷² K. J. Laidler and C. Pegis, *Proc. Roy. Soc.*, 1957, **241**, A, 80.

⁷³ K. J. Laidler, *Can. J. Chem.*, 1956, **34**, 1107.

⁷⁴ D. C. Grahame, *J. Chem. Phys.*, 1950, **18**, 903.

⁷⁵ D. C. Powell and W. M. Latimer, *J. Chem. Phys.*, 1951, **19**, 119.

⁷⁶ R. M. Noyes, *J. Amer. Chem. Soc.*, 1962, **84**, 513.

⁷⁷ E. Gleuckauf, *Trans. Faraday Soc.*, 1964, **60**, 572.

⁷⁸ R. H. Stokes, *J. Amer. Chem. Soc.*, 1964, **86**, 979.

⁷⁹ K. J. Laidler and J. S. Muirhead-Gould, *Trans. Faraday Soc.*, 1966, **62**, 944.

⁸⁰ W. A. Millen and D. W. Watts, *J. Amer. Chem. Soc.*, 1967, **89**, 6051.

⁸¹ D. L. Beveridge and G. W. Schnuelle, *J. Phys. Chem.*, 1975, **79**, 2562 and 2566.

⁸² M. H. Abraham and J. Liszi, *J.C.S. Faraday I*, 1978, **74**, 1604 and 2858.

rotation and polarisability of the solvent molecules in the high electric field gradients at the surface of the ions. Even accepting the somewhat questionable significance of the dielectric constant of a region containing, perhaps, only four to six solvent molecules, such calculations require a more precise theory of dielectric phenomena in polar, and H-bonded, media than is presently available.⁸³⁻⁸⁷ Moreover, such treatments are insensitive to the variety of different ion-solvent molecule interactions that are possible. For example, the strong $\text{Ag}^+ - \text{CH}_3\text{CN}$ interactions cannot be accounted for readily by this approach; nor can differences in sign of trends in the behaviour of anions and cations with increasing ionic size.

Results from more explicit calculations of the interactions of the ion and nearest-neighbour solvent molecules have also been reported. In the simplest case, the solvent molecules are represented by dipoles,^{67,88-92} and only electrostatic interactions considered. The calculations have been extended by improving the representation of the charge distribution of the solvent molecules either as a multipole⁹³ or an array of point charges.^{94,95} In addition, the effects of dispersion forces,⁹⁵ induced dipolar interactions,⁹⁵ solvent-solvent interactions,^{67,88-95} and varying co-ordination numbers and geometries^{95,96} have been considered.

The calculations as described above all give results in quite good agreement with experiment. However, closer examination shows that there are still considerable problems with the precise representation of the more important intermolecular interactions. This can be simply illustrated by consideration of the values for the free energy of hydration, $\Delta G^\circ_{\text{h}}$, of Na^+ calculated by different authors. $\Delta G^\circ_{\text{h}}(\text{Na}^+)$ is defined by equation (9), where $\mu^\circ_{\text{aq}}(\text{Na}^+)$ and $\mu^\circ_{\text{g}}(\text{Na}^+)$

$$\Delta G^\circ_{\text{h}}(\text{Na}^+) = \mu^\circ_{\text{aq}}(\text{Na}^+) - \mu^\circ_{\text{g}}(\text{Na}^+) \quad (9)$$

represent the standard chemical potentials of Na^+ in water and in the gas phase, respectively. The value of $\mu^\circ_{\text{g}}(\text{Na}^+)$, calculated by equation (10), in which the

$$\mu^\circ_{\text{g}}(M^{\dot{z}+}) = \frac{N_A \cdot (Ze)^2}{8\pi\epsilon_0 r} \quad (10)$$

symbols have their usual meanings, depends critically upon the values used for the ionic radius, r , of Na^+ in the gas phase. Various authors have used values for r ranging from the crystal radius^{67-69,82} (0.95 Å for Na^+) to the van der Waals

⁸³ P. Debye, *Handb. Radiol.*, 1925, **6**, 618, 680.

⁸⁴ F. Booth, *J. Chem. Phys.*, 1951, **19**, 391, 1327, 1615.

⁸⁵ A. D. Buckingham, *J. Chem. Phys.*, 1956, **25**, 428.

⁸⁶ F. E. Harris and B. J. Alder, *J. Chem. Phys.*, 1953, **21**, 1031.

⁸⁷ J. G. Kirkwood, *J. Chem. Phys.*, 1939, **7**, 911.

⁸⁸ D. D. Eley and M. G. Evans, *Trans. Faraday Soc.*, 1938, **34**, 1093.

⁸⁹ D. D. Eley and D. C. Pepper, *Trans. Faraday Soc.*, 1941, **37**, 581.

⁹⁰ S. Goldman and R. G. Bates, *J. Amer. Chem. Soc.*, 1972, **94**, 1476.

⁹¹ S. Goldman and L. R. Morse, *Can. J. Chem.*, 1975, **53**, 2695.

⁹² P. R. Tremaine and S. Goldman, *J. Phys. Chem.*, 1978, **82**, 2317.

⁹³ A. D. Buckingham, *Discuss Faraday Soc.*, 1957, **24**, 151.

⁹⁴ E. J. W. Verwey, *Rec. Trav. Chim.*, 1942, **61**, 127.

⁹⁵ J. S. Muirhead-Gould and K. J. Laidler, *Trans. Faraday Soc.*, 1966, **62**, 944.

⁹⁶ W. Veillard, *J. Amer. Chem. Soc.*, 1977, **99**, 7194.

radius^{78,90-92} (1.32 Å for Na⁺),⁷⁸ giving values for $\mu^{\circ}_{\text{g}}(\text{Na}^+)$ ranging from 174 to 122 kcal mol⁻¹. The resulting values of $\Delta G^{\circ}_{\text{h}}(\text{Na}^+)$ are, however, all within a few kcal mol⁻¹ of 103 kcal mol⁻¹. Thus calculated values of $\mu^{\circ}_{\text{aq}}(\text{Na}^+)$, which are the significant quantities in solution, range from 19⁷⁸ to 71 kcal mol⁻¹.⁸² This variation of more than 50 kcal mol⁻¹ for $\mu^{\circ}_{\text{aq}}(\text{Na}^+)$, and corresponding variations for other ions, have particularly serious implications for calculations of $\Delta G^{\circ}_{\text{tr}}$ values for transfer of electrolytes among solvents. It is far larger than, for example, the $\Delta G^{\circ}_{\text{tr}}$ values of the sodium halides among the various solvents. Clearly the numerical results of such calculations must be approached with caution.

Recently a number of relevant calculations using more advanced quantum mechanical techniques have been reported.⁹⁶⁻¹⁰⁶ These methods should ultimately lead to acceptable calculations, but the data available thus far are too sparse to assess the present situation accurately.

While the quantitative success of 'a priori' calculations is limited, the development of the various representations of ionic solvation is extremely illuminating. They have highlighted the importance of ion-solvent molecule interactions, and the difficulties in the calculations arise essentially from lack of precision in the representation of the various types of interactions involved.

The problems associated with 'a priori' calculations, combined with the relative success of qualitative considerations of properties such as the solvent acidity or basicity, have led a number of workers to propose empirical methods of estimating changes in ion-solvent molecule interactions. One such approach involves the use of linear free-energy relationships.¹⁰⁷⁻¹¹² That is, a correlation is sought between the variation in the solvation parameters and one or more experimental parameters selected to represent various properties of the solvent molecules. For example, the solvent's donor number (DN)^{49,111} and acceptor number¹¹⁰ may be used to represent the solvent's Lewis basicity and acidity respectively.

The success of these relationships is variable, and depends upon the degree of

⁹⁷ E. Clementi and H. Popkie, *J. Chem. Phys.*, 1973, **57**, 1077.

⁹⁸ H. Kristenmacher, H. Popkie, and E. Clementi, *J. Chem. Phys.*, 1973, **57**, 1689.

⁹⁹ A. Gupta and C. N. R. Rao, *J. Phys. Chem.*, 1973, **77**, 2888.

¹⁰⁰ M. Urban, S. Pavlick, V. Kello, and J. Mardiakova, *Collect. Czech. Chem. Commun.*, 1975, **40**, 587.

¹⁰¹ M. Salomon, *Can. J. Chem.*, 1975, **53**, 3194.

¹⁰² M. S. Goldenberg, P. K. Kraus, and S. K. F. Luk, *Can. J. Chem.*, 1975, **53**, 1007.

¹⁰³ G. C. Lie, E. Clementi, and M. Yoshimine, *J. Chem. Phys.*, 1976, **64**, 2314.

¹⁰⁴ R. Woolin, F. A. Houle, and W. A. Goddard, *Chem. Phys.*, 1976, **14**, 461.

¹⁰⁵ M. D. Newton, *J. Chem. Phys.*, 1977, **67**, 5535.

¹⁰⁶ P. Claverie, J. P. Daudley, J. Langlot, B. Pullman, D. Piazzola, and M. Huron, *J. Phys. Chem.*, 1978, **82**, 405.

¹⁰⁷ I. A. Koppel and V. A. Palm, 'Adv. in Linear Free Energy Relationships,' ed. N. B. Chapman and J. Shorter, Plenum, New York, 1972.

¹⁰⁸ W. R. Fawcett and T. M. Krygowski, (a) *J. Amer. Chem. Soc.*, 1975, **97**, 2143; (b) *Aust. J. Chem.*, 1975, **28**, 2115.

¹⁰⁹ W. R. Fawcett and T. M. Krygowski, *Can. J. Chem.*, 1976, **54**, 3283.

¹¹⁰ U. Mayer, *Pure Appl. Chem.*, 1979, **51**, 1697.

¹¹¹ V. Gutmann and R. Schmidt, *Coord. Chem. Rev.*, 1974, **12**, 263.

¹¹² E. M. Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253, 3261, 3267.

similarity between the interactions in the ion-solvent system and that used to obtain the relevant solvation parameter. Thus correlations involving the silver halides in acetonitrile and the solvent donor number were poor,^{108a} because the strong Ag^+ -MeCN interaction is absent in the system used to obtain the donor number.¹¹¹ However, the predictive nature of such correlations gives them considerable utility in dealing with changes in solvation parameters (ΔG° , ΔH° , ΔS°) among single-component solvent systems (but not binary mixed solvents; see below).

A second approach to the problem is the use of stability constants for complex formation between an ion and different solvent molecules.^{25,52,113} Thus if a solvent B, acting as a ligand, forms complexes MB, MB₁, MB₂, etc. with an ion M in a second solvent A, the values of the stability constants K_i of the various complexes give a measure of the difference between the strengths of the M-B and M-A interactions (*cf.* Section 3, on ion-solvent interactions in the gas phase). The approach is somewhat limited by the necessity of knowing K_i values for the various ions and solvent pairs of interest, many of which are not readily experimentally accessible. However, it implicitly takes account of the ion-solvent molecule interactions operating in the system of interest. Moreover, it provides a suitable basis for calculating the contribution to $\Delta G^\circ_{\text{tr}}$, $\Delta H^\circ_{\text{tr}}$, and $\Delta S^\circ_{\text{tr}}$ of changes in the co-ordination sphere of the ions, the importance of which is clear from the above discussion, and from gas-phase data (Section 3).

A consideration of solvation in terms of co-ordination equilibria is particularly illuminating when the transfer of electrolytes between two solvents is studied over the whole composition range of solvent compositions from one solvent, through solvent mixtures, to the other solvent. Consider initially the implications of a simplified model in which changes in the properties of the electrolytes arise entirely from changes in the co-ordination sphere. That is, interactions between the solvent molecules in the bulk solvent, and between the co-ordinated ion and the bulk solvent, are taken to be constant. It can be readily shown,²⁵ using simple concepts of competitive equilibria, that under these conditions $\Delta G^\circ_{\text{tr}}(\text{M})$ for transfer of an ion M from solvent A to solvent B is given by equation (11), and to binary mixtures of A and B by equation (12). In equations

$$\Delta G^\circ_{\text{tr}}(\text{M}) = -RT \ln \beta'_n \quad (11)$$

$$\Delta G^\circ_{\text{tr}}(\text{M}) = -nRT \ln \phi_A - RT \ln \left[1 - \sum_{i=1}^n \beta'_i \left(\frac{\phi_B}{\phi_A} \right)^i \right] \quad (12)$$

(11) and (12), n is the co-ordination number of M, and β'_i represent the equilibrium products for the equilibria (13), with the concentrations of A and B being



expressed as ideal volume fractions, ϕ (which may be simply related to concentrations based on the molar concentration scale).²⁵ Equation (11) is identical to,

¹¹³ A. K. Covington and K. E. Newman, *Pure Appl. Chem.*, 1979, **51**, 2041 and refs therein.

and equation (12) closely related to, equations derived by Covington and co-workers,¹¹³ the extra terms in their equation resulting from their attempt to use a more general model.

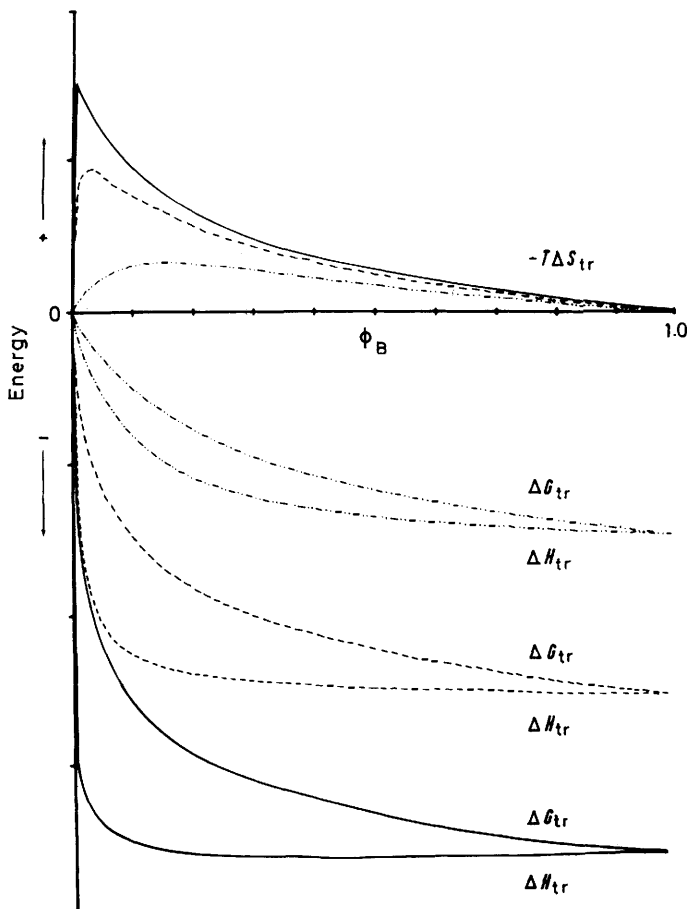


Figure 1 Variations in $\Delta G_{\text{tr}}^{\circ}$, $\Delta H_{\text{tr}}^{\circ}$, and $-T\Delta S_{\text{tr}}^{\circ}$ predicted by the co-ordination mode for varying β'_i values: β'_i (—) > β'_i (- - -) > β'_i (- · - · - ·)

Figure 1 shows the variation of $\Delta G_{\text{tr}}^{\circ}(\text{M})$ calculated from equation (12) for transfer from a poorer solvent A to a better solvent B. There is a monotonic decrease in $\Delta G_{\text{tr}}^{\circ}(\text{M})$, with the decrease being most pronounced in the neighbourhood of $\phi_{\text{B}} = 0$. As the strength of M-B interactions increases relative to those of M-A (*i.e.* β'_i increase), the overall $\Delta G_{\text{tr}}^{\circ}(\text{M})$ increases, and the rate of decrease of $\Delta G_{\text{tr}}^{\circ}(\text{M})$ in the neighbourhood of $\phi_{\text{B}} = 0$ also increases. This rapid decrease in $\Delta G_{\text{tr}}^{\circ}(\text{M})$ results from preferential inclusion of B in the co-ordination

sphere of M, the composition of which may be calculated by equation (14), in which $n_B (= n - n_A)$ is the number of B molecules in the co-ordination sphere. Equation (14) also follows from a standard treatment of successive chemical

$$\frac{n_B}{n} = \frac{1}{n} \left\{ \sum_{i=1}^n i \beta'_i \left(\frac{\phi_B}{\phi_A} \right)^i \left[1 + \sum_{j=1}^n \beta'_j \left(\frac{\phi_B}{\phi_A} \right)^j \right]^{-1} \right\} \quad (14)$$

equilibria.²⁵ It may be readily shown from equation (14) that, as β'_i increases, the degree of preferential inclusion of B in the co-ordination sphere of M also increases.

While the increasing degree of preferential solvation with increasing β'_i leads to increasingly favourable $\Delta G^\circ_{\text{tr}}(\text{M})$ values, the situation becomes increasingly unfavourable with respect to $\Delta S^\circ_{\text{tr}}(\text{M})$ in the solvent mixtures. This is because of the creation of a non-random distribution of solvent molecules in the co-ordination sphere of A. The magnitude of these configurational effects (S_c) is given by equation (15)¹⁶ in which x_A and x_B refer to the mole fractions of A and

$$S_c = -n_A R \ln \left(\frac{n_A}{n x_A} \right) - n_B R \ln \left(\frac{n_B}{n x_B} \right) \quad (15)$$

B in the bulk solvent (and n_A/n and n_B/n are the corresponding mole fractions in the co-ordination sphere of the ion M). Obviously, S_c approaches zero as $x_B \rightarrow 0$ or $x_B \rightarrow 1$, and will pass through a minimum at some intermediate composition unless there is no preferential solvation ($\beta'_i = 1$), in which case it remains at zero. As β'_i increase, and hence n_B/n becomes increasingly different from x_B , the minimum in S_c increases in magnitude and shifts towards $x_B = 0$ (see Figure 1), leading to increasingly unfavourable $\Delta S^\circ_{\text{tr}}(\text{M})$ in the mixtures.

$\Delta H^\circ_{\text{tr}}(\text{M})$ values may be readily calculated from $\Delta G^\circ_{\text{tr}}(\text{M})$ and $\Delta S^\circ_{\text{tr}}(\text{M})$ via equation (16). Qualitatively, the behaviour is similar to that of $\Delta G^\circ_{\text{tr}}(\text{M})$, except

$$\Delta H^\circ_{\text{tr}}(\text{M}) = \Delta G^\circ_{\text{tr}}(\text{M}) + T \Delta S^\circ_{\text{tr}}(\text{M}) \quad (16)$$

that $\Delta H^\circ_{\text{tr}}$ values are more negative in the mixtures, because of the unfavourable contribution of $\Delta S^\circ_{\text{tr}}(\text{M})$ to the $\Delta G^\circ_{\text{tr}}(\text{M})$ values (Figure 1).

Equations (11), (12), and (14) may be made rigorous by the inclusion of solvent activities instead of volume fractions, and activity coefficients of the various species $\text{MA}_{n-i}\text{B}_i$ involved in the equilibria, to allow for changing interactions between $\text{MA}_{n-i}\text{B}_i$ and the bulk solvent (including the effects of varying solvent dielectric constant on the energies of $\text{MA}_{n-i}\text{B}_i$). Estimation of the latter, however, is a formidable task, and it is more instructive to look at differences between experimental results and those calculated from the idealised model in terms of effects not included in the calculations. In the following section the results in Tables 4–7 for four different mixed solvent systems are discussed. Extension to other solvent systems is straightforward.

The DMSO-PC system (Table 7) should most closely approximate to the model solvent system. Thus, both are dipolar aprotic solvents, their mutual heats

of mixing are small,¹¹⁴ and their dielectric constants, although not equal, are high. Moreover, the β'_i for DMSO complexes of a variety of cations have been measured in PC.^{26,309,52} Figure 2 shows the variation of $\Delta G^\circ_{\text{tr}}$, $\Delta H^\circ_{\text{tr}}$, and

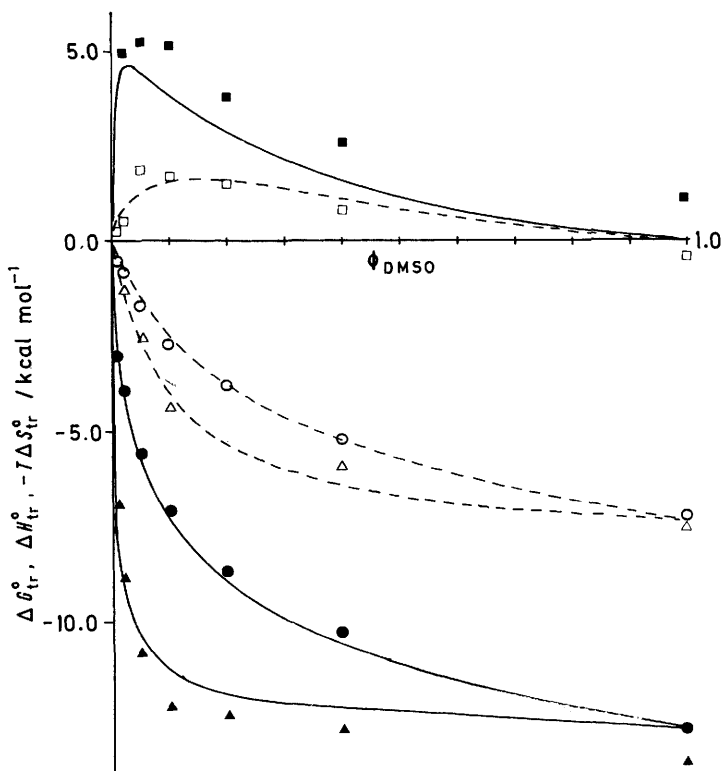


Figure 2 Comparison of $\Delta G^\circ_{\text{tr}}$ (○), $\Delta H^\circ_{\text{tr}}$ (△), and $-298\Delta S^\circ_{\text{tr}}$ (□) of NaCl (open) and AgCl (closed) with the calculated values for Na^+ (---) and Ag^+ (—) vs. ϕ_{DMSO} for PC + DMSO.

$-298\Delta S^\circ_{\text{tr}}$ for NaCl and AgCl from PC to PC + DMSO mixtures. Also included are values calculated from equations (12)–(17), from the measured β'_i for Ag^+ –DMSO and Na^+ –DMSO complexes⁵² (assuming anion effects to be small—Tables 1–3, 7).

The degree to which the simple treatment described above accounts for the variation of $\Delta G^\circ_{\text{tr}}$, $\Delta H^\circ_{\text{tr}}$, and $\Delta S^\circ_{\text{tr}}$ values is striking (similar agreement exists for LiCl). Particularly noteworthy are the predictable maxima in $-298\Delta S^\circ_{\text{tr}}$ and the almost exact agreement of the $\Delta G^\circ_{\text{tr}}$ values. It is also interesting to note the magnitudes of the $-298\Delta S^\circ_{\text{tr}}$ values which can result from preferential solvation:

¹¹⁴ J. Courtôt-Coupez and C. Madec, *Compt. Rend.*, 1973, 277, 15.

5 kcal mol⁻¹ for AgCl (a value of 10 kcal mol⁻¹ would be expected for Ag⁺ salts in mixtures of PC with DMTF).⁵² Similarly good agreement between calculated and experimental results has been found for $\Delta G^\circ_{\text{tr}}$ of Eu²⁺, Yb²⁺, Eu³⁺, and Yb³⁺ in PC + DMSO mixtures,^{30b} and for a variety of cations in other mixed non-aqueous solvent systems,^{25,52} accounting for $\Delta G^\circ_{\text{tr}}$ values as large as 49 kcal mol⁻¹.

Quantitative agreement with theory of $\Delta G^\circ_{\text{tr}}$ values is always more likely than for $\Delta H^\circ_{\text{tr}}$ and $\Delta S^\circ_{\text{tr}}$ values. According to an earlier suggestion by Feakins,¹¹⁵ and a detailed analysis by Ben Naim,¹¹⁶ changes in solvent-solvent interactions in the bulk solvent (solvent structure) brought about by the ions will have a significantly larger influence on the enthalpy and entropy than on free energy values. This may be seen, in particular, in the results for mixed aqueous + organic mixtures. These solvent systems also display considerable deviations from ideality,¹¹⁷⁻¹²⁰ and there exists the possibility of H-bonded interactions between co-ordinated solvent molecules and the surrounding solvent molecules. Variations of $\Delta G^\circ_{\text{tr}}$, $\Delta H^\circ_{\text{tr}}$, and $-T\Delta S^\circ_{\text{tr}}$ for representative electrolytes in H₂O + MeCN, H₂O + DMSO, and H₂O + MeOH are shown in Figures 3 and 4.

Considering the data for the H₂O + MeCN system (Figure 3, Table 4), it is clear that preferential solvation makes a significant contribution to the $\Delta G^\circ_{\text{tr}}$, $\Delta H^\circ_{\text{tr}}$, and $\Delta S^\circ_{\text{tr}}$ values. Thus for AgCl, the sharp decrease in $\Delta G^\circ_{\text{tr}}$ and $\Delta H^\circ_{\text{tr}}$, and increase in $-298\Delta S^\circ_{\text{tr}}$ at low ϕ_{MeCN} results from the expected preferential solvation of Ag⁺ by MeCN,^{16a,25,51} whereas the rapid increase in $\Delta G^\circ_{\text{tr}}$ and $\Delta H^\circ_{\text{tr}}$, and the maximum in $-298\Delta S^\circ_{\text{tr}}$ at low $\phi_{\text{H}_2\text{O}}$ (*i.e.* as $\phi_{\text{MeCN}} \rightarrow 1$), clearly reflect preferential hydration of the anions. Similarly, preferential hydration of Na⁺ and Cl⁻ would account for the sharp drop in $\Delta G^\circ_{\text{tr}}$ and $\Delta H^\circ_{\text{tr}}$ and the maxima in $-298\Delta S^\circ_{\text{tr}}$ values on addition of small amounts of water to MeCN.

The relatively simple variations in ΔG_{tr} are in qualitative agreement with behaviour expected from simple consideration of co-ordination by the two solvent components, but the variations in $\Delta S^\circ_{\text{tr}}$ and $\Delta H^\circ_{\text{tr}}$ are more complex. These terms show features expected from preferential co-ordination, as discussed above, but they are superimposed on large monotonic variations which are largely compensating. In view of Ben Naim's analysis,¹¹⁶ and the insensitivity of the variations to the nature of the electrolyte, it is reasonable to ascribe the compensating variations in $\Delta H^\circ_{\text{tr}}$ and $-298\Delta S^\circ_{\text{tr}}$ to changes in solvent structure, *i.e.* to changes in solvent-solvent interactions in the bulk solvent. These effects, particularly reflected in the large negative entropies of transfer, are typical

¹¹⁵ D. Feakins and P. Watson, *J. Chem. Soc.*, 1963, 4734.

¹¹⁶ A. Ben Naim, 'Water and Aqueous Solutions. An Introduction to a Molecular Theory', Plenum Press, New York, 1974.

¹¹⁷ A. M. Von Vierk, *Z. Anorg. Chem.*, 1950, **261**, 283.

¹¹⁸ M. E. Fox and K. P. Whittingham, *J.C.S. Faraday I*, 1975, **71**, 1407.

¹¹⁹ S. Y. Lam and R. L. Benoit, *Can. J. Chem.*, 1974, **52**, 718.

¹²⁰ J. Timmermans, 'The Physico-Chemical Constants of Binary Systems', Vol. 4, Interscience, New York, 1959.

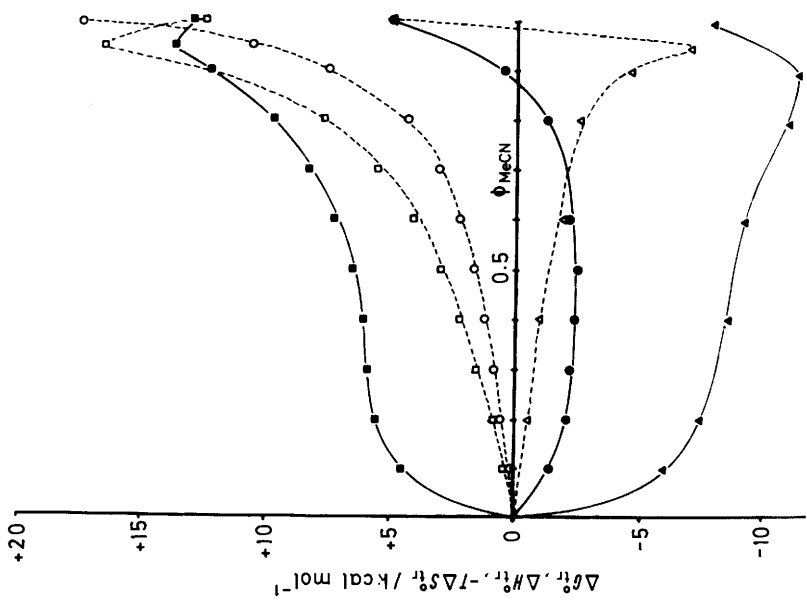


Figure 3 MeCN+H₂O; ΔG°_{tr} , ΔH°_{tr} , and $-298\Delta S^{\circ}_{tr}$ values for NaCl (---) and AgCl(——) vs. ϕ_{MeCN} .

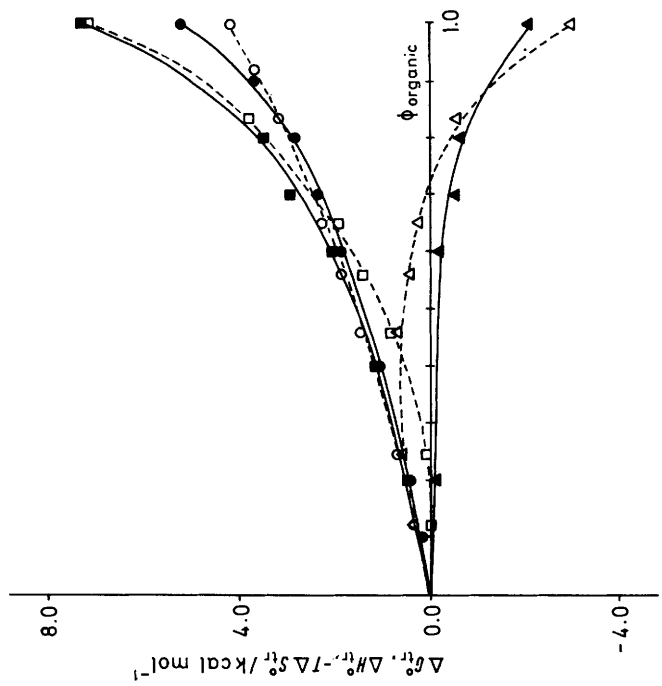


Figure 4 ΔG°_{tr} (O), ΔH°_{tr} (Δ), and $-298\Delta S^{\circ}_{tr}$ (\square) for NaCl in H₂O + MeOH (---, open) and H₂O + DMSO (——, closed) vs. $\phi_{organic}$ component.

of the transfer of electrolytes from water to non-aqueous solvents, especially dipolar aprotic solvents (Table 3).

The variations in $\Delta G^\circ_{\text{tr}}$, $\Delta H^\circ_{\text{tr}}$, and $-298\Delta S^\circ_{\text{tr}}$ for electrolytes in $\text{H}_2\text{O} + \text{DMSO}$ and $\text{H}_2\text{O} + \text{MeOH}$ solvent systems (Figure 4) do not show any indications of preferential solvation. Particularly notable in this context is the absence of anything resembling a maximum in the $-298\Delta S^\circ_{\text{tr}}$ values. The lack of preferential solvation is confirmed by the results of spectroscopic studies of ion solvation in these systems,^{25,121-123} which indicate that the compositions of the co-ordination spheres of the ions differ only slightly from those of the bulk solvent. This lack of preferential solvation is clearly not the result of equality of ion-solvent molecule interactions, as may be seen from the overall $\Delta G^\circ_{\text{tr}}$ values and, for example, from trends in $\Delta G^\circ_{\text{tr}}$ for different anions with a given cation and *vice versa*. These indicate that DMSO, and to a lesser extent, MeOH, are both better Lewis bases than H_2O (and hence interact more strongly with cations), and that water interacts more strongly with anions.

In the case of $\text{H}_2\text{O} + \text{MeOH}$ mixtures, the lack of preferential solvation may be the result of the averaging of the acidity and basicity of the component solvents over all of the solvent molecules through intermolecular hydrogen bonding.²² Thus a MeOH molecule hydrogen bonded to an H_2O molecule transmits part of its extra Lewis basicity to the water molecule, and correspondingly becomes more acidic.

In $\text{DMSO} + \text{H}_2\text{O}$ mixtures, two effects may be important. First, the very strong interactions between H_2O and DMSO molecules, as seen in the large negative deviations from Raoult's Law,⁴⁹ will mitigate against preferential solvation. Thus, for example, preferential solvation of cations by small amounts of DMSO in water requires disruption of strong H_2O -DMSO hydrogen bonds. In support of this it has been shown that the variations in $\Delta G^\circ_{\text{tr}}$ values in $\text{DMSO} + \text{water}$ mixtures can be satisfactorily accounted for by equation (13) if solvent activities rather than concentrations are used.²⁵ Secondly, the Lewis basicity of DMSO molecules in $\text{H}_2\text{O} + \text{DMSO}$ mixtures could be transmitted through H-bonds, as discussed above for $\text{H}_2\text{O} + \text{MeOH}$ mixtures, thus further reducing the probability of preferential cationic solvation in these mixtures. This reasoning has been used to account for the results of n.m.r. experiments, which indicate that the proton is preferentially hydrated over most of the composition range in $\text{DMSO} + \text{H}_2\text{O}$ mixtures.¹²⁴

Again in both the $\text{DMSO} + \text{H}_2\text{O}$ and $\text{MeOH} + \text{H}_2\text{O}$ mixtures the steady increase of $-298\Delta S^\circ_{\text{tr}}$ with decreasing water content of the solvent, and the partly compensating $\Delta H^\circ_{\text{tr}}$ values, are evident in Figure 4. These apparently reflect changes in solvent structure, as discussed above.

¹²¹ A. Clausen, A. A. El-Harakany, and H. Schneider, *Ber. Bunsenges. Phys. Chem.*, 1973, **77**, 994.

¹²² L. S. Frankel, T. R. Stengle, and C. H. Langford, *Can. J. Chem.*, 1968, **46**, 3183.

¹²³ M. Holtz, H. Weingartner, and H. G. Wertz, *J.C.S. Faraday I*, 1977, **73**, 71.

¹²⁴ P. T. McTigue and A. P. Watkins, *Aust. J. Chem.*, 1972, **25**, 777.

5 Conclusion

The discussion above has been in terms of specific examples, but a number of common features can be distinguished.

(i) Differences between the interactions of various ions in the different solvents are largely the result of differences in interactions between the ions and the immediate neighbour solvent molecules. These mainly involve differences in the enthalpies of interaction, and so are reflected in the $\Delta G^\circ_{\text{tr}}$ and $\Delta H^\circ_{\text{tr}}$ values of electrolytes between single-component solvents (Tables 1 and 2).

(ii) The $\Delta S^\circ_{\text{tr}}$ values between single-component solvents are relatively independent of the electrolyte for simple inorganic electrolytes (Table 3), and predominantly reflect changes in solvent structure. These changes are greatest on transfer from water to the various non-aqueous solvents, but large effects are also apparent on transfer from other H-bonding solvents such as MeOH, formamide, and *N*-methylformamide to dipolar aprotic solvents. Variations in solvent structure involve changes in enthalpies, as well as entropies of the solvent molecules, and so affect $\Delta H^\circ_{\text{tr}}$ values of electrolytes. These contributions to $\Delta S^\circ_{\text{tr}}$ and $\Delta H^\circ_{\text{tr}}$ values, which have a common origin in changes in solvent structure, are largely compensating in their contributions to $\Delta G^\circ_{\text{tr}}$ values. Thus $\Delta G^\circ_{\text{tr}}$ values largely reflect differences in direct ion-solvent interactions.

(iii) The behaviour of electrolytes containing large organic ions such as R_4N^+ , Ph_4As^+ , and BPh_4^- is typical of that observed for non-electrolytes. Thus, on transfer from water, they show negative $\Delta G^\circ_{\text{tr}}$ values and positive $\Delta H^\circ_{\text{tr}}$ and $\Delta S^\circ_{\text{tr}}$ values.

(iv) In mixed solvent systems, preferential solvation causes very characteristic variations in $\Delta G^\circ_{\text{tr}}$, $\Delta H^\circ_{\text{tr}}$, and $\Delta S^\circ_{\text{tr}}$ values. Of these, minima in $\Delta S^\circ_{\text{tr}}$ (maxima in $-T\Delta S^\circ_{\text{tr}}$) are, perhaps, the most diagnostic. These effects are predictable, and in many cases calculable from stability constants of the appropriate complexes between the ions and the solvent molecules. The $\Delta G^\circ_{\text{tr}}$ values, and the extent of preferential solvation, can be modified by strong solvent-solvent interactions between the component solvents, or by an averaging of the Lewis acidities and basicities of the component solvents by a co-operative mechanism, such as H-bonding. Structural changes in mixed solvents also contribute to $\Delta H^\circ_{\text{tr}}$ and $\Delta S^\circ_{\text{tr}}$ values by amounts which largely compensate, as in single-component systems. Thus the $\Delta G^\circ_{\text{tr}}$ variations in mixed solvents are commonly simpler than those of $\Delta H^\circ_{\text{tr}}$ and $\Delta S^\circ_{\text{tr}}$.