Entropies of Transfer of Tetra-alkylammonium Ions from Water to Methanol, Dimethylformamide, and Acetonitrile

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Summary For transfer from water to methanol or dimethylformamide (DMF), $\Delta S^\circ_t(M^+)$ is independent of M^+ for $M^+ = K^+, Rb^+$, and Cs^+; if $M^+ = R_4N^+$ the value of $\Delta S^\circ_t(M^+)$ is greater the greater the size of R, thus reflecting the structure-making tendencies of the larger R_4N^+ ions in aqueous solution.

FOLLOWING the important work of Criss, Held, and Luksha,[1] it has been concluded[2] that '. . . . the entropy of transfer of a pair of ions from one solvent to another does not depend greatly on the pair of ions transferred,' and hence that trends in ΔG°_t will follow those in ΔH°_t even[3] for the tetra-alkylammonium ions.

Values of ΔH°_t are known[4] for the transfer of numerous pairs of ions from water to methanol and to DMF, and have been determined in the present work for transfer to acetonitrile. Corresponding values of ΔG°_t have also been determined in the present work (*cf.* refs. 5 and 6) and have been combined with the ΔH°_t values to yield the ΔS°_t values given in the Table. It is now possible to test the validity of the above conclusions[2,3] over a much wider range of cations than previously studied.

TABLE

Single ion entropies of transfer (on the mole fraction scale), relative to $\Delta S^\circ_t(Me_4N^+) = 0$, *in cal* K^{-1} *mol*$^{-1}$ *at* 298 *K*.

Solvent:	Water	Methanol[a]	DMF[a]	Acetonitrile[b]
K^+	0	−19·1[c]	−15·4	−14·1
Rb^+	0	−16·4[c]	−14·9	−12·8
Cs^+	0	−15·0[c]	−13·3	
Me_4N^+	0	0	0	0
Et_4N^+	0	11·3	14·8	16·4
$Pr^n_4N^+$	0	24·5	30·7	32·6
$Bu^n_4N^+$	0	36·7	44·0	47·0
Ph_4As^+[d]	0	22	27	
Cl^-	0	− 5·4[e]	−24·8[d,f]	
Br^-	0	− 6·7[e]	−28·4[d,f]	
I^-	0	− 8·5	−28·3	−26·6
ClO_4^-	0	− 8·4	−25·8	−24·0
Ph_4B^-[d]	0	+15	+12	

[a] Enthalpies of transfer from ref. 4. [b] Enthalpies of transfer, this work. [c] Free-energy data from ref. 6. [d] Free-energy data from R. Alexander, A. J. Parker, J. H. Sharp, and W. E. Waghorn, *J. Amer. Chem. Soc.*, 1972, **94**, 1148, and from I. M. Kolthoff and M. K. Chantooni, *J. Amer. Chem. Soc.*, 1971, **93**, 7104. [e] Free-energy data from A. L. Andrews, H. P. Bennetto, D. Feakins, K. G. Lawrence, and R. P. T. Tomkins, *J. Chem. Soc.* (*A*), 1968, 1486. [f] Free-energy data from J. Courtot-Coupez, M. le Demezet, A. Laouenan, and C. Madec, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1971, **29**, 21.

For transfer from water to methanol and to DMF, values of $\Delta S^\circ_t(M^+ + X^-)$ in cal $K^{-1}mol^{-1}$ average *ca.* −24 and −41 respectively, if the cations are restricted to K^+, Rb^+, and Cs^+ (X^- may be Cl^-, Br^-, I^-, or ClO_4^-). This relative constancy of ΔS°_t with respect to M^+ breaks down completely for transfer involving the R_4N^+ cations. The very large positive values of ΔS°_t for transfer from water to all three nonaqueous solvents no doubt reflect the increasing structure-making properties of the larger

R_4N^+ ions in aqueous solution; for all three transfers ΔH°_t increases but ΔG°_t decreases as the R_4N^+ ions become larger.

Even for transfers amongst the non-aqueous solvents in the Table, values of ΔS°_t $(M^+ + X^-)$ are not constant if $M^+ = R_4N^+$; for example $\Delta S^\circ_t(Bu^n{}_4N^+) - \Delta S^\circ_t(Me_4N^+)$ is 7 and 10 cal K^{-1} mol^{-1} for transfer from methanol to DMF and to acetonitrile respectively. The so-called constancy of $\Delta S^\circ_t(M^+ + X^-)$ is thus restricted to $M^+ = K^+$, Rb^+, or Cs^+. If ions such as R_4N^+ (and also Ph_4As^+ and Ph_4B^-) are considered then the ΔS°_t values are no longer independent of the pair of ions transferred, at least for transfers between water, methanol, DMF, and acetonitrile. Similar behaviour is observed when solvents ethanol and Me_2SO are used, but data for these two solvent systems are less complete than for those in the Table.

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