Use of Cryptates in the Determination of Single-ion Free Energies of Transfer Between Two Solvents

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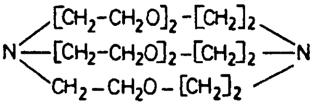
Summary Free energies of transfer of the chloride (or azide) anion from water to methanol are obtained from sodium chloride (or azide) solutions containing a cation binding reagent.

There has been considerable effort in attempting to evaluate the energies and enthalpies of single-ion transfer between two solvents. A variety of extrathermodynamic assumptions have been proposed to split the medium effect for electrolytes into values for individual ions.[1,2] This communication deals with a new method to achieve this result. Its main feature lies in using cryptates, a class of very powerful cation binding reagents recently discovered by Lehn *et al.*[3] The cryptate (**1**) forms a very stable complex with the sodium cation in both water and methanol (logarithmic stability constants: 5·4 and $\geqslant 8$, respectively[4]). We assume that the cation is completely embedded within the organic cryptate molecule, and may therefore be considered as abstracted from the solution. Short-range solute–solvent interactions are indeed removed in this way; long-range interactions, beyond the cryptate molecule, are assumed to be negligible. In support of this assumption is the fact that such complexes[5] are not detected by the appropriate ion-selective glass membrane electrodes.[6]



(1)

The free energies of transfer ΔG_t° of sodium chloride and azide from water to methanol have been measured by a method first described by Grunwald.[7] The procedure uses a series of water–methanol mixtures ranging from pure water to pure methanol (mole fraction of water: x_1). For each of them, the derivative: $d\Delta G_t^\circ/dx_1$ may be computed from the composition of the vapour over the solvent before and after the addition of the electrolyte. $\Delta G_t^\ominus$ values result from integration from $x_1 = 0$. The pertinent formula (equation 9, ref. 8) contains two terms allowing for ionic activity coefficient. These corrections are $< 8\%$ at any electrolyte concentration (0·03—0·08 molal) on account of the high dielectric constants of the solvent mixtures presently studied. Their variation on complexing the sodium cation is even smaller ($< 3\%$). On the whole, they will be neglected at this stage.

TABLE. Single-ion free energies of transfer, $\Delta G_t^\ominus$, and ΔG_t^* (in parentheses) from water to aqueous methanol (kJ mol^{-1} on the mole fraction scale at 25 °C; mean accuracy: 20%)

x_1	Cl^-[a]	N_3^-	$AsPh_4^+$[a]
1·00	0·0(0·0)	0·0(0·0)	0·0(0·0)
0·88	5·4(5·4)	2·1(3·3)	−11·3(−12·5)
0·73	7·9(8·4)	5·0(7·5)	−17·5(−19·2)
0·54	9·6(11·3)	8·4(10·4)	(−23·0)
0·31	11·3(12·5)	12·1(12·9)	−25·5(−25·0)
0·00	12·9(12·9)	17·1(16·3)	−29·3(−25·9)

[a] ΔG_t^* values from ref. 9.

The vapour was analysed by g.l.c. by a technique already described.[8] We first checked that the addition of the cryptate molecule (*ca.* 0·1 molal) to the pure solvent mixture did not change the composition of the vapour. The electrolyte (*ca.* 0·05 molal) was then added and the vapour analysed again. $\Delta G_t^\ominus$ values thus obtained for NaCl or NaN_3 were assigned to single ions Cl^- or N_3^-, and are compared in the Table with the analogous values, ΔG_t^*, obtained without cryptate, using the extrathermodynamic assumption $\Delta G_t^\ominus(AsPh_4^+) = \Delta G_t^\ominus(BPh_4^-)$.

The agreement between both methods is fortuitously much better than expected from the experimental errors. Comparisons with previous literature values show reasonable agreement with the results of Parker,[1] Popovych,[10] and Case and Parsons:[11] 12·3, 9·03, and 16·7 (compared with 12·9) kJ mol^{-1}, respectively, for Cl^-. Older results of De Ligny[12] (29·3), Feakins[13] (33·4), and Strehlow[14] (23·4) are not consistent with these values. We may also deduce that $\Delta G_t^\ominus(AsPh_4^+) = -29{\cdot}3$ and $\Delta G_t^\ominus(Na^+) = -0{\cdot}4$ kJ mol^{-1} by subtraction. There is again good agreement between these values and, respectively:[9] $\Delta G_t^*(AsPh_4^+) = -25{\cdot}9$ and $\Delta G_t^*(Na^+) = -0{\cdot}4$ kJ mol^{-1}, indirectly supporting the validity of the assumption about $AsPh_4^+$ and BPh_4^-. That the free energies of solvation of BPh_4^- and $AsPh_4^+$ are nearly equal in water and methanol in spite of different enthalpies, ΔH_t, of transfer[15] must therefore be due to some compensation in enthalpies ΔH_t and entropies $T\Delta S_t$, as pointed out by one referee.

We tentitatively conclude that cryptates may open a route to a reliable scale of single-ion free energies of transfer.

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