Calculation of Heats of Transfer of Some Zwitterions in Water from Considerations of Volume Changes

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THE molar heat of transfer Q^* for a binary liquid mixture can be obtained from measurements of the Soret coefficient (σ) and of activity coefficients (γ) on the molality (m) scale by using the relationship,

$$\sigma = \frac{1}{m}\left(\frac{\mathrm{d}m}{\mathrm{d}T}\right)_{\text{stat.}} = \frac{Q^*}{RT^2\left(1 + \frac{\partial \ln \gamma}{\partial \ln m}\right)_T} \qquad (1)$$

The suffix "stat." indicates that the concentration gradient is measured in the stationary state. Arguments based on linear non-equilibrium thermodynamics, and the Onsager equations, with due regard for the reference frame with respect to which all flows are measured, show that Q^* has the following significance. If one mole of solute is transferred from left to right across a solvent-fixed reference plane in an isothermal system, then Q^* is the heat which must be absorbed by the region to the left of this plane so that the temperature and pressure of the region remain constant.[1] Attempts to relate Q^* to other physical properties of the system have been concerned mainly with the part played by inter-particle forces.[2-4] There is little doubt that, for a series of similar solutes in the same solvent, Q^* usually increases with the size of the solute molecule, and here is described a possible method of calculating the contribution of this size effect based purely on macroscopic considerations. As has been stated, Q^* has themodynamic significance only when related to a solvent-fixed reference plane. The only reference plane of experimental significance is one fixed with respect to the laboratory. Transfer of a diffusing entity from left to right across the solvent-fixed frame is associated with a transfer of volume across this plane. In consequence, the solvent-fixed frame moves with respect to the laboratory-fixed frame. It is assumed here that the experimental heat of transfer includes, as a component, the amount of heat which must be supplied to the region lying to the left of this plane in order to return the solvent-fixed plane to its original position in the laboratory-fixed frame of reference. An alternative but somewhat less precise description is that the volume transferred out of this region leaves a void volume, or available volume, into which the remaining molecules can expand with an increase in entropy and an absorption of heat which contributes to the experimental value of Q^*. If the effective molar volume of the unsolvated solute is V_s, and if it carries with it n molecules of strongly-bound solvent of effective molar volume V_e, the passage of the solute across the reference plane leaves a void volume $(V_s + n\,V_e)$ behind. However, an equal number of solvent molecules must be transferred in the opposite direction because of the definition of the reference plane. If these have an effective molar volume V_0, then the net volume transfer, associated with the movement of one mole solute, is $[V_s + n(V_e - V_0)]$. The region to the left of the plane can expand into this available volume with an entropy increase of $(\partial S/\partial V)_T[V_s + n(V_e - V_0)]$, which is associated with a heat absorption of $T(\partial S/\partial V)_T[V_s + n(V_e - V_0)]$. From Maxwell's equations, and the definitions of the coefficients of isobaric expansion (α), and of isothermal compression (χ), it follows that,

$$(\partial S/\partial V)_T = \alpha/\chi$$

The ratio α/χ for water is approximately 0·11 cal. ml.$^{-1}$ deg.$^{-1}$, appreciably smaller than for most other liquids. At 300°K, therefore, $T\ (\partial S/\partial V)_T$ for pure water is about 33 cal. ml.$^{-1}$ Assuming that this value applies to reasonably dilute aqueous solutions, heats of transfer of the order of those observed in practice namely, around 1 kcal. mole^{-1}, would require a change in available volume $[V_s + n(V_e - V_0)]$ of the order of 30 ml. mole^{-1}. This is obviously a reasonable requirement.

In aqueous solutions, it is known that water molecules held in a solvate sheath occupy a smaller volume than do those in free water. Consequently $(V_e - V_0)$ is negative, and a small heavily-hydrated solute could show a negative volume-change contribution to the heat of transfer. If n decreases with temperature then Q^* should increase with temperature, and a qualitative explanation of the observation that Q^* increases with temperature for some solutes and not for others,[5] could therefore be given in terms of a change in solvation number with temperature. Another possible explanation, based upon an assumed "structure-breaking" effect of the solvated solute upon the solvent, has already been discussed.[5,6]

The hydration number is not known precisely, and so an attempt was made to calculate $TV_s(\alpha/\chi)$, a quantity which should give an upper limit to the measured value of Q^* for any solute for which this volume effect predominates. The quantity V_s is not the partial molar volume of the solute, because this already includes effects associated with the solute–solvent interactions, nor is it the molar volume derived from measurements of crystal density since this includes a van der Waals volume contribution. It is necessary to estimate the size of the void left when a solute molecule is removed, and it seems reasonable to use for this the molar volume derived from a scale model of the molecule. The volumes in the Table were derived from measurements on "Catalin" models. Comparisons of $TV_s(\alpha/\chi)$ with Q^*, using the value of α/χ appropriate to water, are given in this Table for glycine, and the three possible N-methyl substituted glycines.

TABLE

Solute	Molar volume V_s (ml. mole^{-1})	$TV_s\alpha/\chi$ (cal. mole^{-1} at 20°)	Approx. exptl. heat of transfer at 25° (cal. mole^{-1})
Glycine[a]	22·1	710	210—240
N-Methylglycine[b]	28·0	900	~600
NN-Dimethylglycine[b]	33·8	1090	~900
NNN-Trimethylglycine[b]	40·5	1290	1200—1500

[a] Above 1 M, ref. 5; [b] ref. 7.

N-Trimethylglycine, in common with other betaines, is not believed to be appreciably solvated, and the calculated and experimental values are close. Glycine has an apparent molal volume which is less than the crystal volume, and considerably less than the apparent molar volume of its uncharged isomer glycolamide. It is therefore assumed to be solvated. Consequently $[V_s + n(V_e - V_0)] < V_s$, and this could account for the above difference between Q^* and $TV_s\,\alpha/\chi$. The experimental values for the N-methyl- and NN-dimethyl-glycines are also less than the calculated values, the discrepancy being smaller in the second case, and a possible explanation could be given in terms of decreasing solvation as the degree of substitution increases.

The possible importance of this volume effect in determining Q^* clearly cannot be overlooked. It certainly gives results of the correct order of magnitude for aqueous solutions of solutes of the type considered here, but is not immediately applicable to binary solutions whose components are completely miscible. For these it is possible to devise an alternative treatment in terms of a mole-fixed reference frame. With the assumption that the volume available on removal of a component is equal to its partial molar volume, it can be shown that the component with the larger partial molar volume should have a positive heat of transfer, and that the heats of transfer so calculated obey the relationship:

$$N_1Q_1^* + N_2Q_2^* = 0$$

Since however the theory is concerned essentially with a calculation of the contribution of "*available volume*" changes to the heats of transfer, both this assumption and, to a lesser extent, that made (in the Table) in calculating V_S from models, must be incorrect. For example, a small solute molecule in an assembly of large solvent molecules could conceivably move without causing any change in the volume available to the latter, *i.e.*, without contributing to Q^*. All the solutes considered in the Table have molecules appreciably larger than the solvent water molecules, and the model volume appears to be a not unreasonable estimate of V_S in these cases.

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[1] *Cf.*, H. J. V. Tyrrell, "Diffusion and Heat Flow in Liquids," Butterworth, London, 1961.

[2] I. Prigogine, L. de Brouckère, and R. Amand, *Physica*, 1950, **16**, 577, 851.

[3] K. G. Denbigh, *Trans. Faraday Soc.*, 1962, **48**, 1.

[4] J. N. Agar, *Adv. Electrochem. Electrochem. Eng.*, 1963, **3**, 96.

[5] H. J. V. Tyrrell and M. Zaman, *J. Chem. Soc.*, 1964, 6216.

[6] M. Kennerley, H. J. V. Tyrrell, and M. Zaman, *J. Chem. Soc.* (*A*), 1966, 1041.

[7] M. Kennerley, unpublished results.