26. *The Thermochemistry of Solutions. Part IV. The Heat of Solution of Sodium Chloride in Methanol–Water Mixtures.*

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The heat of solution of sodium chloride at high dilution in methanol–water mixtures has been measured in an adiabatic calorimeter previously described. The results support the view that the ions are preferentially solvated by water but that methanol is not excluded from the solvent sheath except when the water concentration is comparatively high.

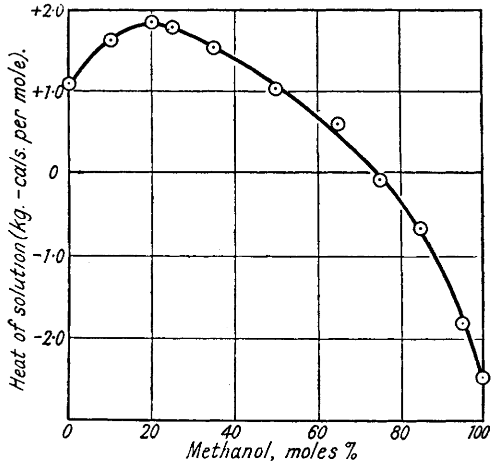
THE object of the present work was to obtain, by thermochemical measurements, evidence as to the composition of the solvent sheath around the ions of a salt dissolved in a mixed solvent. The differential electrostatic attraction of ions for molecules of varying polarisability must be expected to lead to a higher concentration of the more polarisable solvent round the ions of an electrolyte dissolved in such a mixture. Whether and in what circumstances this preferential attraction may cause the molecules of the more polarisable solvent to monopolise the solvent envelope round the ions is a matter for experimental investigation. The limited evidence available (*e.g.*, Shaw and Butler, *Proc. Roy. Soc.*, 1930, *A*, **129**, 519, from the effect of lithium chloride on the activities of ethanol–water mixtures; Hughes and Hartley, *Phil. Mag.*, 1933, **15**, 610, from the effect of small additions of water on the conductivity of non-aqueous electrolytes) suggests that the exclusion of the less polarisable solvent is less complete than might perhaps have been expected, but it seemed worth while to seek confirmatory evidence from an independent source.

If the heat of solution (extrapolated to infinite dilution) of sodium chloride in methanol–water mixtures is measured, the variation of heat of solvation with changing solvent composition is revealed, and the results may be expected to give some indication of the nature of the solvent sheath in relation to the bulk composition of the solvent. The result of such experiments is described below.

EXPERIMENTAL.

The calorimeter for heats of *dilution* described in Part I (J., 1934, 1362) was used; blank experiments showed that the silver lid was entirely efficient in excluding solvent vapour from the salt in the inner compartment before dissolution began. The only substantial modification in the apparatus consisted in the installation of an improved multiple-junction thermel for showing temperature differences between bath and calorimeter. The increased sensitivity and mechanical stability of the new thermel justify a short description of its construction.

The thermel consisted of alternate strips of copper and constantan ribbon rolled from wire (S.W.G. 28) to a breadth of about 1 mm. It was wound round a series of ebonite formers, rectangular in cross section (16 mm. × 6 mm.), which converged radially from the surface of the submarine to within 1 mm. of the outer surface of the rotating calorimeter. A thread, 1 mm. wide, was made in each former with a very thin file so that an average of seven couples per cm. length of former was made possible. Eight such formers were mounted in the upper half of the submarine with Faraday cement, thin strips of mica serving to insulate the outer set of junctions electrically from the submarine. The eight formers, comprising 302 effective thermocouples, were arranged electrically in two groups of four; the constituent members of each group were in series and the two groups in parallel with one another. The resistance of thermel and leads was found to be 48 ohms. With a short-period galvanometer (resistance 12 ohms; sensitivity 500 mm. per microampère) the new thermel showed a sensitivity of 3000 mm. per degree Centigrade on a scale 120 cm. from the galvanometer mirror. This increased sensitivity ($2\frac{1}{2}$ times that of the thermel described in Part I) eliminated the need for a reading microscope, minimised the effect of parasitic potentials in the thermel circuit, and generally simplified the task of maintaining the temperature of the bath equal to that of the calorimeter. The increased rigidity and compactness were also advantageous.



MeOH, moles %.	*C.*	*H.*	H_∞.
10	0·0244	$+1{\cdot}7_1$	$+1{\cdot}6_1$
20	0·0280	$+1{\cdot}9_9$	$+1{\cdot}8_5$
25	0·0203	$+1{\cdot}9_3$	$+1{\cdot}7_9$
,,	0·0213	$+1{\cdot}9_1$	$+1{\cdot}7_7$
35	0·0251	$+1{\cdot}6_2$	$+1{\cdot}4_2$
,,	0·0212	$+1{\cdot}7_2$	$+1{\cdot}5_3$
,,	0·0215	$+1{\cdot}7_2$	$+1{\cdot}5_3$
,,	0·0207	$+1{\cdot}7_6$	$+1{\cdot}5_8$
50	0·0216	$+1{\cdot}2_8$	$+1{\cdot}0_1$
,,	0·0299	$+1{\cdot}3_3$	$+1{\cdot}0_2$
65	0·0295	$+0{\cdot}9_5$	$+0{\cdot}5_6$
,,	0·0234	$+0{\cdot}9_8$	$+0{\cdot}6_3$
75	0·0299	$+0{\cdot}3_3$	$-0{\cdot}1_1$
,,	0·0230	$+0{\cdot}2_9$	$-0{\cdot}1_0$
,,	0·0234	$+0{\cdot}3_0$	$-0{\cdot}0_9$
85	0·0227	$-0{\cdot}2_7$	$-0{\cdot}6_8$
95	0·0188	$-1{\cdot}3_5$	$-1{\cdot}7_5$
,,	0·0232	$-1{\cdot}4_5$	$-1{\cdot}8_9$

The installation of the new thermel was expected to contribute substantially to the effective heat capacity of the calorimeter and to an extent which could not be calculated *a priori*. The heat capacity was therefore re-determined by measuring the heat of solution of sodium chloride in water in the calorimeter and combining the results with the accurate data of Lipsett, Johnson, and Maass (*J. Amer. Chem. Soc.*, 1927, **49**, 935, 1340) for this quantity. The mean of seven determinations at 20° gave a heat capacity of 24·2 cals./degree.

The experimental procedure was identical with that described in Part I. In calculating the results tabulated above, the specific heat of the final solution was taken to be that of the mixed solvent as determined by graphical interpolation from the data of the International Critical Tables. In order to extrapolate the heats of solution obtained to infinite dilution, it is necessary to make some assumption as to the heat of dilution of sodium chloride in methanol–water mixtures. For this purpose the theoretical heat of dilution according to the Born–Bjerrum equation has been employed, Åkerlöf's dielectric-constant data (*ibid.*, 1932, **54**, 4125) for methanol–water mixtures being used. The heats of solution were measured at such low concentrations that the uncertainty caused by this approximation is very unlikely to lead to any appreciable error in the general form of the variation of the heat of solvation with solvent composition.

Results.—In the table, col. 1 shows the composition of the solvent as molar percentage of methanol, col. 2 the concentration of the solution formed (*C*, in moles/l.), col. 3 the heat of solution (*H*, in kg.-cals./mole), and col. 4 the value of the heat of solution corrected to infinite dilution, H_∞. The initial temperature in each experiment was 20° ± 0·1°; at this temperature the heats of solution at infinite dilution in the two pure solvents are $-2{\cdot}5_0$ and $+1{\cdot}0_8$ kg.-cals./mole respectively for methanol and water (cf. Part II), the positive sign corresponding to heat *absorbed*. The error of any single determination is unlikely to exceed 0·1 kg.-cal.; the concordance between duplicate values under the same conditions is usually distinctly better. The mean values of the heat of solution at infinite dilution are plotted against solvent composition in the diagram.

DISCUSSION.

In interpreting the results it is well to bear in mind the relative proportions of ions and solvent molecules present. In a 0·025N-solution of sodium chloride in 95 molar % methanol, the proportions of the molecular species present are of the order of $Na^+ = Cl^- = 1$; $H_2O = 60$; $MeOH = 1000$. In such a solution there are therefore plenty of water molecules available completely to hydrate the ions present. It is observed, however, that, although the heat of solution rises rapidly with increasing concentration of water, in 95% methanol the heat of solution ($-1{\cdot}8_2$ kg.-cals./mole) is still much nearer the value for pure methanol ($-2{\cdot}5_0$ kg.-cals./mole) than that for pure water ($+1{\cdot}0_8$ kg.-cals./mole). A heat of solution midway between that for the pure solvents is not reached until the concentration of the water has increased to about 15 moles %. Without implying any simple proportionality between heat of solvation and composition of the solvent sheath, it is clear that the greater affinity of the ions for water is not sufficient to exclude methanol from the solvent sheath until there is a relatively high proportion of water molecules present. The existence of a maximum in the heat of solution curve suggests, however, that the relationship between heat of solvation and the composition of the solvent sheath cannot be a simple one; we cannot offer an explanation of this unexpected maximum.

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