301. *The Thermochemistry of Solutions. Part III. Heats of Dilution of Electrolytes in Non-aqueous Solvents.*

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THE calorimeter described in Part I has been used to measure the heats of dilution of a number of non-aqueous solutions of electrolytes. The scope of these measurements is more restricted than that of the survey of heats of solution in Part II, and the results are not comparable in accuracy with those obtained by Lange's differential technique (summarised in *Chem. Reviews*, 1931, **9**, 89). Nevertheless, the data, covering 9 salts and 4 solvents, are of value because existing data relate only to aqueous solutions.

The heat of dilution of the ideal electrolyte of the interionic attraction theory should be positive and vary linearly with the square root of the concentration (cf. Wolfenden, *Ann. Reports*, 1932, **29**, 29); actually, however, for aqueous solutions of uni-univalent electrolytes, it is negative at concentrations above about $N/20$ (with a few notable exceptions such as the salts of lithium and of fluorine), and positive only at higher dilutions. Even at the highest dilutions, Lange and his collaborators found that, contrary to theory, the limiting slope of the plot of the integral molar heat of dilution against the square root of the concentration showed small individual variations from salt to salt. The persistence of these individualities down to high dilutions in such a solvent as water might encourage expectations of an even greater diversity of behaviour in non-aqueous solvents of lower dielectric constant. It is accordingly surprising to find that, amongst the non-aqueous solutions investigated, heats of dilution are generally positive over the whole concentration range.

In Table I is given the theoretical limiting slope (Gatty, *Phil. Mag.*, 1931, **11**, 1082) defined by the equation $V_c = A\sqrt{c}$, where V_c is the integral molar heat of dilution (kg.-cals.) of a uni-univalent electrolyte from a concentration c (in mols./l.) down to infinite dilution. The theoretical values of A, which refer to 20°, depend only on the properties of the solvent; owing to the uncertain magnitude of the temperature coefficient of the dielectric constant of the various solvents, the values of A are not of a high order of accuracy. In Table II, col. 1 gives the salt; cols. 2 and 3 the initial and the final concentration, c_1 and c_2 respectively; col. 4 the corresponding heat of dilution (kg.-cals./mol.), *i.e.*, $V_{c_1} - V_{c_2}$; and col. 5 the function $A' = (V_{c_1} - V_{c_2})/(\sqrt{c_1} - \sqrt{c_2})$, whose limiting value at infinite dilution should correspond to A in the theoretical equation. The heat capacities of the solutions have been taken as the sum of those of the constituents.

TABLE I.

Solvent.	A (at 20°).	Solvent.	A (at 20°).
Water	0·46	Nitromethane	0·68
Methyl alcohol	2·61	Nitrobenzene	2·12
Ethyl alcohol	6·49		

TABLE II.

Heats of dilution in methyl alcohol.

Salt.	c_1.	c_2.	$V_{c_1} - V_{c_2}$.	A'.	Salt.	c_1.	c_2.	$V_{c_1} - V_{c_2}$.	A'.
NaCl *	0·094	0·052	0·15	+1·9	NEt_4Br	1·133	0·576	−0·025	−0·083
	0·052	0·036	0·08	+2·1		0·576	0·291	0·004	+0·019
	0·036	0·023	0·10	+2·6		0·480	0·201	0·012	+0·049
	0·023	0·008	$0·2_7$	$+4·_7$		0·291	0·137	0·043	+0·255
NaI	0·408	0·205	0·258	+1·39		0·192	0·095	0·045	+0·34
	0·205	0·094	0·226	+1·55		0·137	0·069	0·072	+0·67
	0·094	0·046	0·16	+1·67		0·095	0·045	0·07	+0·7
	0·046	0·023	0·15	+2·5		0·069	0·034	0·05	+0·7
	0·023	0·011	0·14	+2·9		0·045	0·022	0·12	+1·8
$NaClO_4$	1·415	0·647	0·761	+1·976		0·045	0·022	0·09	+1·4
	0·647	0·287	0·559	+2·08		0·034	0·016	0·07	+1·2
	0·600	0·244	0·577	+2·06		0·016	0·0077	0·11	+2·8
	0·287	0·143	0·370	+2·33	NEt_4NO_3	0·954	0·437	−0·027	−0·09
	0·143	0·067	0·32	+2·67	$AgNO_3$	0·073	0·025	0·18	+1·6
	0·067	0·032	0·23	+2·85	$Ca(NO_3)_2$	0·365	0·164	0·28	+1·4
	0·032	0·016	0·23	+4·4	$CaCl_2$	0·162	0·069	0·65	+2·7
	0·026	0·011	0·19	+3·5					
	0·016	0·008	0·17	+4·6					
	0·008	0·0035	0·12	+4·2					

Heats of dilution in nitromethane.

$NaClO_4$	0·017	0·008	0·06	+1·6	$NEt_4Pic.$	0·025	0·012	0·045	+0·97
$NEt_4Pic.$	0·199	0·097	0·06	+0·43		0·013	0·006	0·055	+1·7
	0·025	0·012	0·045	+0·97					

Heats of dilution in nitrobenzene.

NEt_4ClO_4	0·020	0·0095	0·09	+2·0	$NEt_4Pic.$	0·100	0·050	0·12	+1·3
						0·025	0·0124	0·06	+1·3

Heats of dilution in water.

$NaClO_4$	0·502	0·233	−0·14	−0·62	$AgClO_4$	0·512	0·221	−0·10	−0·41
$AgNO_3$	0·366	0·167	−0·13	−0·60		0·211	0·099	−0·03	−0·2

* The values for sodium chloride are derived from heats of solution measured over a range of concentrations.

In addition to the above quantitative results, two qualitative measurements showed that the heat of dilution of concentrated solutions of tetraethylammonium bromide in water and in ethyl alcohol was negative in both cases.

The most striking feature of the above results is that all the heats of dilution in non-aqueous solvents are positive with the exception of concentrated solutions of the tetraethylammonium salts in methyl and ethyl alcohols. Among the many factors which may cause the magnitude and sign of the heat of dilution of an electrolyte to deviate from the ideal behaviour, and particularly at higher concentrations, important parts must be played by the breaking down of " ion-pairs " and by the higher-order energy terms of the ionic atmosphere. A convenient, if arbitrary, measure of the combined influence of these and similar factors may be obtained from conductivity data by calculating a " true dissociation constant " in the manner described by Davies (J., **1933**, 645). Mr. A. G. Ogston, of this laboratory, has made conductivity measurements, shortly to be published, of electrolytes in methyl and ethyl alcohols at 4°, 15°, and 25°; from the temperature coefficients of the " dissociation constants " derived from these measurements, he has calculated the " heats of dissociation " of nine salts in one or both of these solvents. The only salts showing a negative heat of dissociation are tetraethylammonium bromide, perchlorate, and picrate, whilst five uni-univalent salts with metallic cations show positive heats of dissociation. This positive correlation of sign between heats of dilution and " heats of dissociation " is evidently significant, although no quantitative agreement is to be sought.

The heat of dissociation of an ion-pair is equal to the difference between the sum of the heats of solvation of the two ions and the heat of solvation of the ion-pair. Since it is not unreasonable to suppose that the latter quantity would be small compared with the former, it might be argued that, for a given salt in a range of solvents, negative heats of dissociation are most likely to occur in those solvents where the heat of ion solvation is lowest. On this basis it would be anticipated that, provided the correlation between heats of dilution and heats of dissociation be significant, negative heats of dilution would be observed in solvents where the heats of ionic solvation are lower than usual. In qualitative agreement with this expectation, it is found that negative heats of dilution are confined to the small group of salts whose heats of solution in the given solvent are lower than the corresponding heats of solution in water (cf. Part II). The scope of the measurements recorded in this paper is, however, too restricted for much significance to be attached to this correlation.

It is also interesting to note that, whereas in water the values of A' for uni-univalent salts are always *less* than the theoretical limiting value A, even at the highest dilutions measured by Lange, yet in non-aqueous solutions experimental values greater than A have been observed in two of the solvents studied. It is tempting to relate these deviations from theoretical behaviour to the existence of ion-pairs in solution, since, even in dilute solutions, the tetraethylammonium salts in methyl alcohol (with negative heats of dissociation) give smaller values of A' than the salts with metallic cations (with positive heats of dissociation).

A closer examination of our results shows that the observed facts cannot be interpreted, even qualitatively, in terms of " heats of dissociation," derived from conductivity measurements, so long as these are assumed to be independent of concentration. Inspection shows that A' diminishes in magnitude with increasing concentration irrespective of the sign of the " heat of dissociation." The simple superposition of dissociation (with a heat of dissociation independent of concentration) upon the purely electrostatic heat of dilution would have led one to anticipate that A' would diminish in magnitude with increasing concentration for salts with a negative heat of dissociation (such as the tetra-alkylammonium salts), but that the function would increase with increasing concentration for salts with a positive heat of dissociation.

The failure of the simplified picture to represent the facts is not surprising when it is recalled that Debye and Hückel treated electrolytic solutions as though the electrical contribution to the free energy of ion solvation could be regarded as independent of concentration and written down formally as a series of Born terms for ionic solvation at infinite dilution. In Part II, short-ranges forces and electrical saturation effects have been shown to invalidate the Born expression corresponding to the heats of ionic solvation at infinite dilution. It is therefore reasonable to expect that in concentrated solutions the same two factors will prevent the ionic solvation terms from being independent of concentration.

SUMMARY.

(1) The heats of dilution of a number of salts in methyl and ethyl alcohols, nitromethane, nitrobenzene, and water have been measured.

(2) Negative heats of dilution, which are so common in aqueous solutions, are comparatively rare in non-aqueous solutions.

(3) A positive correlation has been found between negative heats of dilution, on the one hand, and negative heats of dissociation and low heats of ionic solvation, on the other.

(4) The second differential coefficient of the integral molar heat of dilution with respect to the square root of the concentration is found to be negative irrespective of the sign of the heat of dissociation of the electrolyte. The results can therefore not be explained even qualitatively by the simple superposition of incomplete dissociation upon the Debye–Bjerrum theory of heats of dilution.

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