300. *The Thermochemistry of Solutions. Part II. Heats of Solution of Electrolytes in Non-aqueous Solvents.*

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The calorimeter described in Part I (preceding paper) was first used to survey the heats of solution of electrolytes in non-aqueous solvents, concerning which few data are recorded. In this part, the heats of solution of 17 uni-univalent salts (known to be strong electrolytes) in water, methyl alcohol, ethyl alcohol, nitromethane, nitrobenzene, and acetone are described for 50 salt–solvent combinations. All the results are accurate at least to the nearest 0·25 kg.-cal. The theoretical interest of such heats of solution is considerable inasmuch as they can be used to evaluate the heat of solvation of ions, and thus to throw light on the nature of ion–solvent interaction.

The integral molar heat of solution, L_c, is defined as the heat evolved when 1 mol. of solute dissolves in the amount of pure solvent necessary to give a solution of final concentration c; the value of L_c when extrapolated to $c = 0$ is denoted by L_0, the integral molar heat of solution at infinite dilution. The process of solution at infinite dilution may be considered to take place in two stages: (i) 1 mol. of solute is evaporated into a vacuum; (ii) the molecules of rarefied vapour are dissolved in an infinite amount of the pure solvent. The absorption of heat accompanying process (i) is denoted by $+ U$ and may be called the lattice heat; the heat evolved during process (ii), which is the molar heat of solvation,* is denoted by $+ W$. Then

$$L_0 = - U + W \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If the solute is an electrolyte, a free-energy term corresponding to U can be calculated from X-ray and compressibility data for the case when the vapour is assumed to consist of isolated ions. The latter quantity is called the lattice energy G, and is usually assumed to be equal to U. There may be said to be one W term for each ionic species in the crystal; *i.e.*, for a uni-univalent electrolyte, if the rarefied vapour referred to is ionised, $W = W^+ + W^-$, where W^+ and W^- denote the molar heats of solvation of the cation and the anion respectively. Then

$$L_0 = - U + W^+ + W^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The lattice energies of the alkali halides range from 278 kg.-cals./mol. for lithium fluoride to 132 kg.-cals./mol. for cæsium iodide, the accepted values being probably correct to about 2%; in many other cases the lattice energy cannot readily be calculated. Since L_0 can be measured with an accuracy of about 0·1 kg.-cal., errors of 2% in the lattice energy are relatively serious. Another difficulty associated with this equation is that no experimental means has yet been devised for dividing W into its two components W^+ and W^-.

The uncertainties connected with the lattice energies of crystals may be eliminated by measuring the heat of solution of a salt in more than one solvent; *e.g.*,

$$L_{0,\mathrm{MeOH}} = - U + W^+_{\mathrm{MeOH}} + W^-_{\mathrm{MeOH}}$$
$$L_{0,\mathrm{H_2O}} = - U + W^+_{\mathrm{H_2O}} + W^-_{\mathrm{H_2O}}$$

so that, by subtraction, the lattice energy disappears:

$$L_{0,\mathrm{MeOH}} - \mathbf{L}_{0,\mathrm{H_2O}} = (W^+_{\mathrm{MeOH}} + W^-_{\mathrm{MeOH}}) - (W^+_{\mathrm{H_2O}} + W^-_{\mathrm{H_2O}}).$$

By eliminating U in this way, the measurement of L_0 in more than one solvent increases some ten-fold the accuracy with which heat content changes due to ion–solvent interaction may be studied.

Some information is already available as to the free-energy changes associated with ion–solvent interaction from measurements of *E.M.F.*, solubility, vapour pressure, and partition coefficients (see Bell, *Ann. Reports*, 1933, **30**, 16). On the other hand, little is known of the heat-content changes, whose interest is enhanced by Lange's work on heats of dilution, which indicates that specific effects due to the nature of the electrolyte are more marked in this case than in that of the corresponding free-energy changes.

The molecular model which has attracted most attention in the theory of solutions is that of the ion considered as a sphere with a charge uniformly distributed over its surface and immersed in a continuous medium (the solvent). The principal object of the present work was to examine the extent to which the heats of solution of electrolytes conform with this idealised model, first put forward by Born (*Z. Physik*, 1920, **1**, 45). Assuming that an ion of charge ε behaves like a sphere of constant radius a, and that the solvent behaves like

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* This term is conventionally applied to the heat content change accompanying the transfer from a vacuum to the given solvent; it is thus a special case of a "heat of transfer." The term is an unhappy one in so far as the forces envisaged by the Born–Bjerrum equation are not those of solvation in the accepted chemical sense.

a completely homogeneous medium of dielectric constant D, Born calculated the energy required to charge 1 g.-ion in a large volume of solvent as

$$\overline{W}_e^0 = N\varepsilon^2/2DaJ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where W_e^0 represents the energy in cals./g.-ion, J is the mechanical equivalent of heat, and N is Avogadro's number. If the process of charging is regarded as taking place at constant temperature and pressure, $\overline{W}_e^0$ represents a contribution to the partial molar free energy of the electrolyte. Equation (3) can be extended to calculate the electrical contribution to the partial molar free energy of transfer of ions from the rarefied vapour into a solution of limitingly low concentration. This quantity may be regarded as the electrical contribution to the free energy of solvation of the ion and, since the dielectric constant of a vacuum is unity, is given by the equation :

$$\Delta\overline{W}_e^0 = N\varepsilon^2(1 - 1/D)/2DaJ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Free energies of individual ions, as opposed to those of electrolytes, cannot be measured, so this equation is tested by considering an electrolyte containing ν_a, ν_β . . . ions of sorts α, β . . ., of charges z_a, z_β, . . . and of radii a_a, a_β . . . Since the electrolyte as a whole is electrically neutral, $\Sigma\nu_a z_a = 0$, and

$$\Delta\overline{W}_e^0 = \frac{N\varepsilon^2}{2J}\left[\Sigma\frac{\nu_a z_a^2}{a_a}\right]\left[1 - \frac{1}{D}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By using the Gibbs–Helmholtz equation, equation (5) can be converted into an expression for the electrical contribution to the heat of solvation, and if the ionic radii are assumed not to vary with temperature, it becomes the Born–Bjerrum equation (*Z. physikal. Chem.*, 1927, **127**, 369) :

$$\Delta\overline{H}_e^0 = \frac{N\varepsilon^2}{2J}\left[\Sigma\frac{\nu_a z_a^2}{a_a}\right]\left[1 - \frac{1}{D}\left\{1 + \frac{T}{D}\left(\frac{\partial D}{\partial T}\right)_p\right\}\right] \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If the molecular model of Born is accepted, and it is assumed that the heat of solvation of an ion is exclusively due to its electrical charges, $\Delta\overline{H}_e^0$ must represent the true heat of solvation of an electrolyte. The difference between the corresponding values of $\Delta\overline{H}_e^0$ for the same electrolyte in two solvents is the heat of transfer from one solvent to the other, and should, on the above hypothesis, be equal to the difference between the integral molar heat of solution at infinite dilution of the electrolyte in the two solvents. The measurement of heats of solution of electrolytes at high dilution in a range of solvents, therefore, affords a direct test of the Born–Bjerrum equation and of the molecular model on which it is based.

Before proceeding to the results of this experimental test, the grounds on which the ultra-simple Born model is open to criticism may be indicated :

(i) It is not permissible to neglect all forces other than the electrostatic forces round the ion. Not only would other " non-electrical " forces be anticipated on general theoretical grounds, but their existence is demonstrated experimentally by Lannung's experiments (*J. Amer. Chem. Soc.*, 1930, **52**, 68) on the heats of solution of the inert gases in different solvents, which sometimes amount to 3 kg.-cals./mol.

(ii) The Born calculation of the electrostatic energy needed to charge the ion treats the solvent as a continuous medium and neglects its structure. Electrostriction and electrical saturation must both play important parts in altering the properties of the solvent in the immediate vicinity of the ion which is the seat of the greater part of the energy. Further, it is conceivable that ions of different sign will orient the solvent molecules in different ways, and thus lead to characteristic differences between anions and cations.

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* Strictly the expression on the right-hand side ought to include two additional terms: $+ RT^2(\partial \ln V/\partial T)_p - RT$, where V is the molar volume of the pure solvent. The derivation of these terms will be discussed in a later theoretical paper. The latter and larger disappears for heats of transfer, and the former, ranging from 0·05 to 0·2 kg.-cal., is too small to affect the conclusions of the present paper.

(iii) It is difficult to define the radius *a* other than as an electrostatic capacity. The possibility that *a* varies from solvent to solvent is not susceptible to experimental test, since the work of charging an ion cannot be measured directly. This difficulty is also illustrated by trying to assign *a priori* a value of *a* to the picrate ion with its negative phenolic oxygen and three polar nitro-groups.

The results of the present work will be seen to show that the Born–Bjerrum equation for heats of solvation is inadequate. The equation breaks down in relation to the predicted effect both of (i) the dielectric constant of the solvent and of (ii) the radius of the ions. Specific short-range forces seem to be important and, in particular, characteristic differences between cations and anions are suggested by our results.

EXPERIMENTAL.

Materials.—The solvents used were prepared by the technique employed in the researches on conductivity carried out in this laboratory (*Proc. Roy. Soc.*, 1931, **126**, *A*, 84; J., 1931, 201, 215). The salts were recrystallised specimens of a high degree of purity; they were dried to constant weight in an electric oven, reduced pressure being used if they were liable to decomposition.

Heat Capacity.—The heat capacity was calculated from the known heat capacity of calorimeter and air-gap, together with that of the solvent, that of the solute being negligible. The following specific heats at 20° were adopted : water 0·999, methyl alcohol 0·600, ethyl alcohol 0·570, nitromethane 0·400, nitrobenzene 0·350, acetone 0·528.

Extrapolation of Heats of Solution to Infinite Dilution.—The heats of solution were mostly measured at concentrations of *ca.* 0·01*N*. The extrapolation to infinite dilution was carried out by the corrected form of the heat of dilution equation put forward by Scatchard (*J. Amer. Chem. Soc.*, 1931, **53**, 2037) and by Gatty (*Phil. Mag.*, 1931, **11**, 1082). The correction at *N*/100 varies from 0·046 kg.-cal./mol. for water to 0·65 kg.-cal./mol. for ethyl alcohol. The application of a theoretical correction instead of an experimental one introduces an uncertainty which may amount to 0·1 kg.-cal./mol., but this is practically eliminated in the "differential heats of transfer" to be considered later.

In Table I are listed the individual determinations at 20° ± 0·4°, uncorrected for small variations in the initial temperature. Col. 1 gives the electrolyte, col. 2 the concentration *c* in mols./l. of the final solution, col. 3 the observed heat of solution in kg.-cals./mol. (L_c), col. 4 the corresponding value extrapolated to infinite dilution (L_0), and col. 5 the weighted mean value adopted.

TABLE I.

Heats of solution in water.

Salt.	*c.*	L_c.	L_0.	Mean.
LiCl	0·0427	+ 8·476	+ 8·570	$+ 8{\cdot}5_7$
LiPic	0·0080	− 3·776	− 3·735	$- 3{\cdot}7_3$
NaCl	0·0204	− 1·171	− 1·106	−1·08 *
,,	0·0297	− 1·154	− 1·076	
,,	0·0327	− 1·057	− 0·974	
,,	0·0301	− 1·097	− 1·008	
,,	0·0223	− 1·120	− 1·052	
,,	0·0391	− 1·100	− 1·010	
,,	0·0332	− 1·164	− 1·081	
,,	0·0359	− 1·169	− 1·083	
,,	0·0292	− 1·146	− 1·068	
NaBr	0·0142	− 0·041	+ 0·013	+ 0·01
NaI	0·0129	+ 1·538	+ 1·590	+ 1·61
,,	0·0183	+ 1·577	+ 1·639	
NaClO$_4$	0·0045	− 3·536	− 3·507	− 3·51
,,	0·0061	− 3·536	− 3·506	
NaPic	0·0075	− 7·663	− 7·623	− 7·62
NMe$_4$Cl	0·0100	− 1·182	− 1·147	− 1·12
,,	0·0087	− 1·133	− 1·091	
NMe$_4$Br	0·0061	− 6·011	− 5·975	− 5·96
,,	0·0102	− 6·004	− 5·958	
,,	0·0094	− 5·986	− 5·942	
NEt$_4$Cl	0·0058	+ 4·241	+ 4·276	+ 4·23
,,	0·0061	+ 4·150	+ 4·186	
NEt$_4$Br	0·0048	− 1·603	− 1·572	− 1·60
,,	0·0065	− 1·659	− 1·622	
NEt$_4$ClO$_4$	0·0096	− 7·191	− 7·147	− 7·18
,,	0·0101	− 7·269	− 7·223	
NEt$_4$Pic	0·0099	− 7·360	− 7·325	− 7·22
,,	0·0098	− 7·220	− 7·185	
,,	0·0045	− 7·514	− 7·485	
,,	0·0044	− 6·880	− 6·851	
,,	0·0096	− 7·497	− 7·462	
,,	0·0048	− 7·332	− 7·302	
,,	0·0097	− 7·172	− 7·137	
,,	0·0097	− 7·144	− 7·109	
,,	0·0045	− 7·129	− 7·100	

* The measurements of Lipsett, Johnson, and Maass (*J. Amer. Chem. Soc.*, 1927, **49**, 1940) extrapolated to infinite dilution lead to a value of −1·07 kg.-cals. The value −1·08 is obtained from the calculated heat capacity of the calorimeter, 10·52 cals./degree, which is used throughout this paper.

TABLE I (*contd.*).

Heats of solution in methyl alcohol.

Salt.	c.	L_c.	L_0.	Mean.	Salt.	c.	L_c.	L_0.	Mean.
LiCl	0·0078	+12·623	+12·850	+12·3$_8$	KNO_3	0·0092	− 4·443	− 4·185	− 4·1$_9$
,,	0·0110	+12·188	+12·462		NMe_4Cl	0·0079	− 3·395	− 3·147	− 3·18
,,	0·0495	+11·365	+11·944		,,	0·0087	− 3·464	− 3·207	
,,	0·0162	+11·561	+11·892		NMe_4Br	0·0068	− 7·224	− 7·007	− 6·98
,,	0·0080	+12·678	+12·949		,,	0·0086	− 7·205	− 6·962	
LiPic	0·0091	+ 1·043	+ 1·305	+ 1·30	NEt_4Cl	0·0085	+ 0·061	+ 0·301	+ 0·31
NaCl	0·0048	+ 2·394	+ 2·554	+ 2·50	,,	0·0041	+ 0·154	+ 0·321	
,,	0·0536	+ 1·812	+ 2·422		NEt_4Br	0·0051	− 4·558	− 4·370	− 4·38
,,	0·0084	+ 2·236	+ 2·479		,,	0·0051	− 4·580	− 4·392	
,,	0·0107	+ 2·169	+ 2·433		NEt_4ClO_4	0·0101	− 8·512	− 8·253	− 8·24
NaBr	0·0099	+ 3·837	+ 4·096	+ 4·30	,,	0·0104	− 8·479	− 8·220	
,,	0·0043	+ 4·352	+ 4·506		NEt_4Pic	0·0087	− 8·166	− 7·923	
NaI	0·0161	+ 7·158	+ 7·489	+ 7·52	,,	0·0087	− 8·237	− 7·994	− 8·2$_0$
,,	0·0157	+ 7·222	+ 7·548		,,	0·0046	− 8·576	− 8·406	
$NaClO_4$	0·0061	+ 2·346	+ 2·547	+ 2·62	,,	0·0045	− 8·550	− 8·380	
,,	0·0043	+ 2·527	+ 2·696		,,	0·0011	− 8·323	− 8·235	
NaPic	0·0070	− 2·212	− 1·964	− 1·9$_6$	,,	0·0011	− 8·429	− 8·341	
KCl	0·0122	− 1·703	− 1·413	− 1·4$_1$	,,	0·0197	− 8·676	− 8·306	
KBr	0·0121	− 1·357	− 1·067	− 1·0$_7$	,,	0·0196	− 8·567	− 8·197	
KI	0·0129	+ 0·347	+ 0·647	+ 0·6$_5$					

Heats of solution in ethyl alcohol.

Salt.	c.	L_c.	L_0.	Mean.	Salt.	c.	L_c.	L_0.	Mean.
LiCl	0·0072	+12·836	+13·388	+12·9$_3$	KI	0·0100	− 1·3$_9$	− 0·7$_4$	− 0·$_7$
,,	0·0144	+11·765	+12·537		NMe_4Cl	0·0078	− 4·118	− 3·540	− 3·52
,,	0·0158	+12·059	+12·870		,,	0·0076	− 4·064	− 3·499	
LiPic	0·0075	+ 2·408	+ 2·969	+ 2·9$_7$	NMe_4Br	0·0031	− 7·486	− 7·129	− 7·16
NaBr	0·0103	+ 1·952	+ 2·602	+ 2·65	,,	0·0028	− 7·423	− 7·079	
,,	0·0044	+ 2·274	+ 2·702		,,	0·0028	− 7·602	− 7·258	
,,	0·0082	+ 2·062	+ 2·646		NEt_4Cl	0·0049	− 0·929	− 0·475	− 0·52
NaI	0·0095	+ 4·943	+ 5·576	+ 5·8$_0$	,,	0·0047	− 1·008	− 0·567	
,,	0·0091	+ 5·256	+ 5·874		NEt_4Br	0·0056	− 5·736	− 5·249	− 5·26
,,	0·0173	+ 5·168	+ 6·025		,,	0·0056	− 5·763	− 5·276	
,,	0·0095	+ 5·106	+ 5·736		NEt_4Pic	0·0077	− 9·527	− 8·958	− 8·9$_5$
$NaClO_4$	0·0039	+ 0·240	+ 0·642	+ 0·8$_9$	,,	0·0055	− 9·829	− 9·349	
,,	0·0055	+ 0·653	+ 1·133		,,	0·0056	− 9·379	− 8·893	
NaPic	0·0083	− 1·004	− 0·420	− 0·4$_2$	,,	0·0066	− 9·127	− 8·601	

Heats of solution in nitromethane.

Salt.	c.	L_c.	L_0.	Mean.	Salt.	c.	L_c.	L_0.	Mean.
NMe_4Br	0·0046	− 4·142	− 4·097	− 4·12	NEt_4Br	0·0056	− 2·609	− 2·558	− 2·59
,,	0·0051	− 4·181	− 4·133		,,	0·0020	− 2·676	− 2·623	
NEt_4Cl	0·0053	+ 0·563	+ 0·612	+ 0·59	NEt_4ClO_4	0·0096	− 2·510	− 2·443	− 2·43
,,	0·0052	+ 0·526	+ 0·577		,,	0·0095	− 2·484	− 2·417	
					NEt_4Pic	0·0127	− 5·869	− 5·784	− 5·7$_8$

Heats of solution in nitrobenzene.

Salt.	c.	L_c.	L_0.	Mean.	Salt.	c.	L_c.	L_0.	Mean.
NEt_4ClO_4	0·0106	− 2·599	− 2·387	− 2·40	NEt_4Pic	0·0099	− 5·204	− 4·993	− 5·20
,,	0·0096	− 2·475	− 2·266		,,	0·0097	− 5·145	− 4·945	
,,	0·0018	− 2·685	− 2·595		,,	0·0050	− 5·220	− 5·070	
,,	0·0022	− 2·388	− 2·288		,,	0·0049	− 5·237	− 5·086	
,,	0·0199	− 2·640	− 2·344		,,	0·0012	− 5·408	− 5·334	
,,	0·0095	− 2·554	− 2·345		,,	0·0012	− 5·273	− 5·199	
,,	0·0181	− 2·773	− 2·489		,,	0·0066	− 5·369	− 5·197	
,,	0·0206	− 2·598	− 2·293		,,	0·0059	− 5·405	− 5·243	
					,,	0·0132	− 5·389	− 5·145	

Heats of solution in acetone (approx.).

NEt_4Cl, $L_0 = 0{\cdot}0$; NEt_4Br, $L_0 = -3{\cdot}3$ kg.-cals.

DISCUSSION OF RESULTS.

The above results have been collected from work extending over a number of years, during which the apparatus and technique have steadily developed. The standard of accuracy is therefore by no means uniform. The most accurate group of results is that for the tetra-alkylammonium halides, those for tetraethylammonium picrate in all solvents, and for the potassium halides in methyl alcohol, being least accurate.

The results are discussed under two main headings : (1) heats of transfer of electrolytes at high dilution from one solvent to another ; (2) differences between the heats of transfer of two electrolytes having a common ion from one solvent to another, as derived from the most accurate group of results, followed by a general survey of these "differential heats of transfer" derived from the less accurate measurements of the remainder of the electrolytes so far investigated. The first of these headings provides an extensive test of the Born–Bjerrum equation as an expression for molal heats of transfer at high dilution. The second, while illustrating the order of accuracy obtainable with the calorimeter, throws further light on the problem of ion–solvent interaction.

(1) *Heats of Transfer*.—The heats of transfer of electrolytes from one solvent to another, calculated from the values for L_0, are given in Table II, where the symbol $\Delta^{\text{A}}_{\text{B}}$ represents (L_0 in solvent A) — (L_0 in solvent B). The line enclosing the results for the tetra-alkylammonium halides indicates the higher degree of accuracy of this group of measurements. The data for the potassium salts in water are derived from the work of other authors, *viz.*, KCl (Lange and Monheim, *Z. Elektrochem.*, 1930, **36**, 772), KBr and KI (Wust and Lange, *Z. physikal. Chem.*, 1925, **116**, 161), and KNO_3 (Monval, *Ann. Chim.*, 1925, **3**, 72).

TABLE II.

	$\Delta^{\text{MeOH}}_{\text{H}_2\text{O}}$.	$\Delta^{\text{EtOH}}_{\text{H}_2\text{O}}$.	$\Delta^{\text{EtOH}}_{\text{MeOH}}$.	$\Delta^{\text{MeNO}_2}_{\text{H}_2\text{O}}$.	$\Delta^{\text{MeOH}}_{\text{MeNO}_2}$.	$\Delta^{\text{EtOH}}_{\text{MeNO}_2}$.
NMe_4Cl	$-2{\cdot}06 \pm 0{\cdot}08$	$-2{\cdot}40 \pm 0{\cdot}07$	$-0{\cdot}34 \pm 0{\cdot}07$			
NMe_4Br	$-1{\cdot}02 \pm 0{\cdot}05$	$-1{\cdot}20 \pm 0{\cdot}12$	$-0{\cdot}18 \pm 0{\cdot}13$	$+1{\cdot}84 \pm 0{\cdot}05$	$-2{\cdot}86 \pm 0{\cdot}06$	$-3{\cdot}04 \pm 0{\cdot}13$
NEt_4Cl *......	$-3{\cdot}92 \pm 0{\cdot}07$	$-4{\cdot}75 \pm 0{\cdot}12$	$-0{\cdot}83 \pm 0{\cdot}07$	$-3{\cdot}64 \pm 0{\cdot}09$	$-0{\cdot}28 \pm 0{\cdot}04$	$-1{\cdot}11 \pm 0{\cdot}09$
NEt_4Br †......	$-2{\cdot}78 \pm 0{\cdot}06$	$-3{\cdot}66 \pm 0{\cdot}06$	$-0{\cdot}88 \pm 0{\cdot}04$	$-0{\cdot}99 \pm 0{\cdot}06$	$-1{\cdot}79 \pm 0{\cdot}06$	$-2{\cdot}67 \pm 0{\cdot}06$
LiCl...........	$+3{\cdot}8_1$	$+4{\cdot}3_6$	$+0{\cdot}5_5$			
NaCl	$+3{\cdot}5_8$					
NaBr	$+4{\cdot}3_1$	$+2{\cdot}6_4$	$-1{\cdot}6_7$			
NaI...........	$+5{\cdot}9_1$	$+4{\cdot}1_9$	$-1{\cdot}7_2$			
$NaClO_4$	$+6{\cdot}1_3$	$+4{\cdot}4_0$	$-1{\cdot}7_3$			
KCl...........	$+2{\cdot}9_4$					
KBr	$+3{\cdot}9_3$					
KI	$+5{\cdot}7_0$	$+4{\cdot}_3$	$-1{\cdot}_3$			
KNO_3.........	$+4{\cdot}3_1$					
NEt_4Pic ‡ ...	$-0{\cdot}9_8$	$-1{\cdot}7_3$	$-0{\cdot}7_5$	$+1{\cdot}4_4$	$-2{\cdot}4_2$	$-3{\cdot}1_7$
NEt_4ClO_4 § ...	$-1{\cdot}0_6$			$+4{\cdot}7_5$	$-5{\cdot}8_1$	

* $\Delta^{\text{MeNO}_2}_{\text{COMe}_2} = +0{\cdot}6$. † $\Delta^{\text{MeNO}_2}_{\text{COMe}_2} = +0{\cdot}7$. ‡ $\Delta^{\text{PhNO}_2}_{\text{MeNO}_2} = +0{\cdot}5_8$. § $\Delta^{\text{PhNO}_2}_{\text{MeNO}_2} = +0{\cdot}0_3$.

When applied to the heat of transfer of an electrolyte at great dilution between two solvents A and B the Born–Bjerrum expression becomes

$$L_0{}^{\text{A}} - L_0{}^{\text{B}} = \Delta^{\text{A}}_{\text{B}} = \frac{N_0\varepsilon^2}{2J}\left[\Sigma_a \frac{\nu_a z_a{}^2}{a_a}\right]\left[\frac{1}{D_{\text{B}}}\left\{1 + \frac{T}{D_{\text{B}}}\left(\frac{\partial D_{\text{B}}}{\partial T}\right)_p\right\} - \frac{1}{D_{\text{A}}}\left\{1 + \frac{T}{D_{\text{A}}}\left(\frac{\partial D_{\text{A}}}{\partial T}\right)_p\right\}\right] \quad (7)$$

In this expression N_0, J, the ν's, ε^2, and z^2's are positive. The ions cannot be supposed to have a negative electrostatic capacity, and therefore their radii (a) must be assumed to be positive. Thus the sign of $\Delta^{\text{A}}_{\text{B}}$ must be the same as that of the term included in the second square bracket on the right-hand side of equation (7).

The latter term depends only on the physical properties of the solvents A and B. For a given electrolyte, therefore, the heats of solvation in a series of solvents should be proportional to the values given in Table III. Thus for electrolytes the heats of solution in the six solvents should be lowest in water and should increase in the order given in the table. Consequently, the heat of transfer of any electrolyte from a given solvent to one lower in the table must be positive, and to one higher in the table it must be negative.

TABLE III.

Solvent.	$\left[1 - \frac{1}{D}\left\{1 + \frac{T}{D}\left(\frac{\partial D}{\partial T}\right)_p\right\}\right]$.	Solvent.	$\left[1 - \frac{1}{D}\left\{1 + \frac{T}{D}\left(\frac{\partial D}{\partial T}\right)_p\right\}\right]$.
H_2O	1·0045	$PhNO_2$	1·0153
$COMe_2$	1·0071	MeOH.........................	1·0190
$MeNO_2$.........................	1·0073	EtOH	1·0372

Since all the heats of solution observed are low in comparison with the lattice energies, it is clear that heats of solvation (or transfer from vacuum to a given solvent) are always positive, as theory demands. When, however, the transfers from one solvent to another are investigated, a wide discrepancy between observation and theory is revealed. In Table II the signs of the heats of transfer are so arranged that they should all be positive if expression (7) is correct. For almost every pair of solvents both positive and negative heats of transfer are to be found. For a quantitative account of the facts, then, the Born–Bjerrum expression is totally inadequate. Its failure is illustrated in yet another way by considering the differences of the heats of transfer of two salts with a common ion, called for convenience " differential heats of transfer."

(2) *Differential Heats of Transfer.*—In the first place these quantities may be used to test the over-all accuracy of the experimental work, since, if the heats of transfer at high dilution are assumed to be additive properties of the constituent ions, the difference between the heat of transfer of two ions must be independent of the common ion of opposite sign with which they are associated ; alternatively, the assumption of additivity can be tested within the limits of experimental error. In the second place, these values afford indications as to how and why the Born–Bjerrum equation breaks down. The data for certain transfers are given in Table IV.

TABLE IV.

From water to methyl alcohol.

$$\left.\begin{array}{l}{[\mathrm{NMe_4\text{-}NEt_4}]_{\mathrm{Cl}}} = +\,1{\cdot}86 \pm 0{\cdot}15 \\ {[\mathrm{NMe_4\text{-}NEt_4}]_{\mathrm{Br}}} = +\,1{\cdot}76 \pm 0{\cdot}11\end{array}\right\}\begin{array}{l}\text{Mean, } +\,1{\cdot}80 \pm 0{\cdot}13. \\ \text{Obs. diff., } 0{\cdot}10.\end{array}$$

$$\left.\begin{array}{l}{[\mathrm{Cl\text{-}Br}]_{\mathrm{NMe_4}}} = -\,1{\cdot}04 \pm 0{\cdot}13 \\ {[\mathrm{Cl\text{-}Br}]_{\mathrm{NEt_4}}} = -\,1{\cdot}14 \pm 0{\cdot}13\end{array}\right\}\begin{array}{l}\text{Mean, } -\,1{\cdot}09 \pm 0{\cdot}13. \\ \text{Obs. diff., } 0{\cdot}10.\end{array}$$

From water to ethyl alcohol.

$$\left.\begin{array}{l}{[\mathrm{NMe_4\text{-}NEt_4}]_{\mathrm{Cl}}} = +\,2{\cdot}35 \pm 0{\cdot}19 \\ {[\mathrm{NMe_4\text{-}NEt_4}]_{\mathrm{Br}}} = +\,2{\cdot}46 \pm 0{\cdot}18\end{array}\right\}\begin{array}{l}\text{Mean, } +\,2{\cdot}40 \pm 0{\cdot}19. \\ \text{Obs. diff., } 0{\cdot}11.\end{array}$$

$$\left.\begin{array}{l}{[\mathrm{Cl\text{-}Br}]_{\mathrm{NMe_4}}} = -\,1{\cdot}20 \pm 0{\cdot}19 \\ {[\mathrm{Cl\text{-}Br}]_{\mathrm{NEt_4}}} = -\,1{\cdot}09 \pm 0{\cdot}18\end{array}\right\}\begin{array}{l}\text{Mean, } -\,1{\cdot}15 \pm 0{\cdot}19. \\ \text{Obs. diff., } 0{\cdot}11.\end{array}$$

From methyl alcohol to ethyl alcohol.

$$\left.\begin{array}{l}{[\mathrm{NMe_4\text{-}NEt_4}]_{\mathrm{Cl}}} = +\,0{\cdot}49 \pm 0{\cdot}14 \\ {[\mathrm{NMe_4\text{-}NEt_4}]_{\mathrm{Br}}} = +\,0{\cdot}70 \pm 0{\cdot}17\end{array}\right\}\begin{array}{l}\text{Mean, } +\,0{\cdot}60 \pm 0{\cdot}16. \\ \text{Obs. diff., } 0{\cdot}21.\end{array}$$

$$\left.\begin{array}{l}{[\mathrm{Cl\text{-}Br}]_{\mathrm{NMe_4}}} = -\,0{\cdot}16 \pm 0{\cdot}20 \\ {[\mathrm{Cl\text{-}Br}]_{\mathrm{NEt_4}}} = +\,0{\cdot}05 \pm 0{\cdot}11\end{array}\right\}\begin{array}{l}\text{Mean, } -\,0{\cdot}05 \pm 0{\cdot}16. \\ \text{Obs. diff., } 0{\cdot}21.\end{array}$$

From water to nitromethane.

$$[\mathrm{NMe_4\text{-}NEt_4}]_{\mathrm{Br}} = +\,2{\cdot}83 \pm 0{\cdot}11;\quad [\mathrm{Cl} - \mathrm{Br}]_{\mathrm{NEt_4}} = -\,2{\cdot}65 \pm 0{\cdot}15.$$

From nitromethane to methyl alcohol.

$$[\mathrm{NMe_4\text{-}NEt_4}]_{\mathrm{Br}} = -\,1{\cdot}07 \pm 0{\cdot}12;\quad [\mathrm{Cl} - \mathrm{Br}]_{\mathrm{NEt_4}} = +\,1{\cdot}51 \pm 0{\cdot}10.$$

From nitromethane to ethyl alcohol.

$$[\mathrm{NMe_4\text{-}NEt_4}]_{\mathrm{Br}} = -\,0{\cdot}37 \pm 0{\cdot}19;\quad [\mathrm{Cl} - \mathrm{Br}]_{\mathrm{NEt_4}} = +\,1{\cdot}56 \pm 0{\cdot}15.$$

These figures show that, within the limits of experimental accuracy, the independent heat of solvation of the ions of a salt at high dilution may be taken as established to the nearest 0·2 kg.-cal. On grounds of general plausibility, it therefore seems likely that it is exactly true if L_0 is extrapolated back from sufficiently low concentrations.

In order to see what light differential heats of transfer throw on the problem of the failure of the Born–Bjerrum equation, the data are collected in Table V. The results for the tetra-alkyl halides are some 4—5 times as accurate as any of the others tabulated ; mean values are given where more than one was available.

All the pairs of ions in Table V have that ion placed first whose radius in the crystal is the smaller. If, therefore, the Born–Bjerrum equation were correct, not only as regards the influence of the solvents but also in the way it introduces ionic size, it is clear that every differential heat of transfer quoted in the above table should be positive.

As with single heats of transfer, this is clearly not the case. This confirms the inadequacy of the expression, but a surprising feature appears in Tables IV and V. The consideration

TABLE V.

Pair of ions.	$\Delta^{MeOH}_{H_2O}$.	$\Delta^{EtOH}_{H_2O}$.	Δ^{EtOH}_{MeOH}.	$\Delta^{MeNO_2}_{H_2O}$.	$\Delta^{MeOH}_{MeNO_2}$.	$\Delta^{EtOH}_{MeNO_2}$.
$NMe_4^{\cdot}$–$NEt_4^{\cdot}$	$+1{\cdot}81\pm0{\cdot}13$	$+2{\cdot}40\pm0{\cdot}19$	$+0{\cdot}60\pm0{\cdot}16$	$+2{\cdot}83\pm0{\cdot}11$	$-1{\cdot}07\pm0{\cdot}12$	$-0{\cdot}37\pm0{\cdot}19$
Cl′–Br′ *......	$-1{\cdot}09\pm0{\cdot}13$	$-1{\cdot}15\pm0{\cdot}19$	$-0{\cdot}05\pm0{\cdot}16$	$-2{\cdot}65\pm0{\cdot}15$	$+1{\cdot}51\pm0{\cdot}10$	$+1{\cdot}56\pm0{\cdot}15$
Br′–I′	$-1{\cdot}6_0$	$-1{\cdot}5_5$	$+0{\cdot}0_5$			
Cl′–NO_3′......	$-1{\cdot}3_7$					
Cl′–ClO_4′ ...	$-2{\cdot}5_5$			$-8{\cdot}3_9$		
Cl′–Pic′	$-2{\cdot}9_4$			$-5{\cdot}0_8$		
Cl′–I′	$-2{\cdot}3_3$					
$Li^{\cdot}$–$Na^{\cdot}$	$+0{\cdot}2_3$					
$Na^{\cdot}$–$K^{\cdot}$	$+0{\cdot}6_4$	$-0{\cdot}_1$	$-0{\cdot}_4$			
$Na^{\cdot}$–$NMe_4^{\cdot}$...	$+5{\cdot}4_8$					
$Na^{\cdot}$–$NEt_4^{\cdot}$ ...	$+7{\cdot}2_9$	$+6{\cdot}3_0$	$-0{\cdot}7_9$			
Br′–ClO_4′ ...	$-1{\cdot}8_2$	$-1{\cdot}7_6$		$-5{\cdot}7_4$	$+4{\cdot}0_2$	
Br′–Pic′	$-1{\cdot}8_0$	$-1{\cdot}9_3$	$-0{\cdot}1_3$		$+0{\cdot}6_3$	$+0{\cdot}5_0$

* $\Delta^{MeNO_2}_{COMe_2} = +0{\cdot}1$.

of an additional variable, *viz.*, the sign of the ionic charge, makes the deviations more systematic. In five out of the six pairs of solvents that have been given a fair test, it is seen that the differential heats of transfer for pairs of *cations* all have one sign, while the differential heats of transfer of *anions* for the same pair of solvents all have the opposite sign. The case of the solvent pair, methyl and ethyl alcohols, appears to be anomalous in this respect. It may also be objected that the relative sizes of the nitrate, perchlorate, picrate, and iodide ions (where size is to denote electrostatic capacity) are in some doubt owing to lack of spherical symmetry, the dipole moments on the picrate ion, etc. Thus, if the iodide were regarded as smaller than the perchlorate ion, this would cause a failure of the rule for [I–ClO_4] from water to methyl alcohol. Even admitting these uncertainties, it seems that Table V lends support to the view that ionic size often affects the heats of transfer of cations and anions in opposite senses. The evidence is far from conclusive, but the table indicates that the simple calculations of Born have overlooked a factor depending on the sign of the charge on the ion, though the factor may well be due to secondary interactions due to short-range forces.

Another fact that emerges is that Cl–Br has a transfer of smaller numerical magnitude, irrespective of sign, than Br–I; similarly that Li–Na is smaller than Na–K, which in turn is less than NMe_4–NEt_4; this is unexpected, since with increase in absolute ionic size, the differential heats of transfer might be expected to fall off in magnitude. Since the sign of transfer of Cl–Br and Br–I is different from that of the pairs of cations, this may not be a significant observation. Nevertheless, it appears that the Born–Bjerrum equation is definitely wrong in many cases in its prediction as to the effect of ionic size on heats of transfer.

Another tabulation that brings out the anomalous nature of the results is given in

TABLE VI.

L_0 for NMe_4Cl......... $\left.\begin{matrix}H_2O\\-1{\cdot}12\end{matrix}\right\}\xrightarrow{0\cdot81}\left.\begin{matrix}MeNO_2\\-1{\cdot}93\end{matrix}\right\}\xrightarrow{1\cdot25}\left.\begin{matrix}MeOH\\-3{\cdot}18\end{matrix}\right\}\xrightarrow{0\cdot34}\left.\begin{matrix}EtOH\\-3{\cdot}52\end{matrix}\right\}$

L_0 for NMe_4Br ...... $\left.\begin{matrix}MeNO_2\\-4{\cdot}12\end{matrix}\right\}\xrightarrow{1\cdot84}\left.\begin{matrix}H_2O\\-5{\cdot}96\end{matrix}\right\}\xrightarrow{1\cdot02}\left.\begin{matrix}MeOH\\-6{\cdot}98\end{matrix}\right\}\xrightarrow{0\cdot18}\left.\begin{matrix}EtOH\\-7{\cdot}16\end{matrix}\right\}$

L_0 for NEt_4Cl......... $\left.\begin{matrix}H_2O\\+4{\cdot}23\end{matrix}\right\}\xrightarrow{3\cdot64}\left.\begin{matrix}MeNO_2\\+0{\cdot}59\end{matrix}\right\}\xrightarrow{0\cdot28}\left.\begin{matrix}MeOH\\+0{\cdot}31\end{matrix}\right\}\xrightarrow{0\cdot31}\left.\begin{matrix}COMe_2\\0{\cdot}0\end{matrix}\right\}\xrightarrow{0\cdot52}\left.\begin{matrix}EtOH\\-0{\cdot}52\end{matrix}\right\}$

L_0 for NEt_4Br......... $\left.\begin{matrix}H_2O\\-1{\cdot}60\end{matrix}\right\}\xrightarrow{0\cdot99}\left.\begin{matrix}MeNO_2\\-2{\cdot}59\end{matrix}\right\}\xrightarrow{0\cdot71}\left.\begin{matrix}COMe_2\\-3{\cdot}3\end{matrix}\right\}\xrightarrow{1\cdot08}\left.\begin{matrix}MeOH\\-4{\cdot}38\end{matrix}\right\}\xrightarrow{0\cdot88}\left.\begin{matrix}EtOH\\-5{\cdot}26\end{matrix}\right\}$

$\Delta[NMe_4–NEt_4]$ ...... $H_2O\xrightarrow{+1\cdot81}MeOH\xrightarrow{+0\cdot60}EtOH\xrightarrow{+0\cdot37}MeNO_2$

$\Delta[Cl–Br]$ .... $H_2O\xrightarrow{-1\cdot09}MeOH\xrightarrow{-0\cdot05}EtOH\xrightarrow{-1\cdot46}COMe_2\xrightarrow{-0\cdot1}MeNO_2$

Table VI. On the not unreasonable assumption that the heat of transfer of the smaller halogen ions would predominate over those of the large tetra-alkylammonium ions, it would be expected that the gradation of solvents would be the same for all the above salts; the variations in order show that the heat of transfer of anion and cation must be comparable in magnitude.

The significant feature of the differential heats of transfer for [Cl–Br] is the sharp transition from water to the alcohols, and later that from the alcohols to the non-hydroxylic solvents. If the water molecule is regarded as having two hydroxylic hydrogen atoms, these figures suggest a correlation between the heats of solvation of halogen ions and the number of hydroxylic hydrogen atoms per solvent molecule.

We may summarise our conclusions as follows: (1) The Born–Bjerrum equation for heats of transfer of electrolytes at great dilution from one solvent to another is totally inadequate. (2) The failure is apparent in the case of one electrolyte throughout a variety of solvents, and this shows that the term involving the solvent properties is at fault. (3) The equation also fails to predict the effect of ionic size on the magnitude of heats of transfer. (4) Some effects are specific and may indicate the importance of short-range forces; in particular, co-ordination between anions and hydroxylic hydrogen atoms may be a significant factor. (5) There are indications of characteristic differences between the heats of solvation of cations and anions.

Conclusions (1)—(3) are not unexpected on general theoretical grounds, although the magnitude of the deviations could not have been predicted.

In a later paper it is proposed to discuss the theory of ion-solvent interaction in greater detail.

SUMMARY.

1. The heats of solution of seventeen uni-univalent salts have been measured at high dilution in a series of solvents.

2. The experimental results have been shown to be quite inconsistent with the Born–Bjerrum equation for the heat of solvation of ions.

3. The nature of the discrepancies is discussed.

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