

905. *Studies in Ion Solvation in Non-aqueous Solvents and their Aqueous Mixtures. Part II.*¹ *Properties of Ion Constituents.*

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The molar free energies of transfer of some halogen acids and alkali chlorides, from water to 10 wt. % and 43.12 wt. % methanol-water mixtures, are separated into values for the ion constituents by extrathermodynamic assumptions. The values so obtained are explained by a structural theory of ion solvation. The general considerations are tentatively extended to the remainder of the range of methanol-water mixtures. Acidity functions in alcohols, acetone, and dioxan, and their mixtures with water are briefly discussed and interpreted.

GRUNWALD, BAUGHMAN, and KOHNSTAM² studied the rate of change of free energy of solvation with solvent composition for a large number of electrolytes in 50 wt. % dioxan-water, and, by an ingenious method, divided these quantities into values for single ions. According to simple electrostatic theory, the free energies of solvation of all ions should increase as the dioxan content of the mixture increases, but these authors showed that, although this is true for anions other than large organic ones, the behaviour of cations, including the proton, is the reverse of this.

In this paper we shall first obtain similar quantities for single ions in methanol-water mixtures, using a completely different method.

From the results in Part I,¹ we may determine the free energies of transfer (ΔG_t°) of

¹ Part I, Feakins and Watson, *J.*, 1963, 4686.

² Grunwald, Baughman, and Kohnstam, *J. Amer. Chem. Soc.*, 1960, **82**, 5801.

the pairs of ions H^+Cl^- , H^+Br^- , and H^+I^- , from water to (a) 10 wt. % and (b) 43.12 wt. % methanol-water mixtures, in any chosen standard state. Let ${}^wE^\circ$ and ${}^sE^\circ$ be the standard e.m.f. values of the cell



It will be convenient throughout to consider all transfers as being made from water to some other solvent medium, so that

$$\Delta G_t^\circ = -F\Delta E_t^\circ, \quad (1)$$

where

$$\Delta E_t^\circ = {}^sE^\circ - {}^wE^\circ.$$

The molar standard state has been adopted here, because, as in a closely related problem,³ there is strong circumstantial evidence that volume fraction statistics are fundamental in relation to mixed-solvent studies. Table 1 therefore shows these values

TABLE 1.

Electrolyte	ΔG_t° (cal.)	ΔH_t° (cal.)	$-T\Delta S_t^\circ$ (cal.)	Electrolyte	ΔG_t° (cal.)	ΔH_t° (cal.)	$-T\Delta S_t^\circ$ (cal.)
<i>Water to 10% methanol transfer</i>				<i>Water to 43.12% methanol transfer</i>			
HCl	180	330	-170	HCl	701	880	-180
HBr	125	320	-195	HBr	438	570	-130
HI	58	200	-200	HI	12	190	-180
LiCl	341	900	-560	LiCl	1520	650	870
NaCl	454	480	-25	NaCl	2066	680	1390
KCl	484	290	+195	KCl	2256	375	1880

of ΔG_t° on the molar scale, together with values for the alkali chlorides, calculated from Åkerlöf's e.m.f. data.⁴ The values of ΔG_t° for the halogen acids are accurate to ± 7 cal. or slightly better; those for the alkali chlorides are assumed to be of the same accuracy.

A positive value of ΔG_t° means that the pair of ions is in a lower free-energy state in water than in the mixed solvent. This is qualitatively predicted from Born's equation,

$$\Delta G_t^\circ = \frac{Ne^2}{2} \left[\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w} \right] \left[\frac{1}{r_c} + \frac{1}{r_a} \right], \quad (2)$$

where ϵ_s and ϵ_w are the dielectric constants of the mixed solvent and of water, and r_c and r_a are the radii of the cation and anion. All the values in Table 1 are positive.

Equation (2) may be tested in two ways. First, for a given electrolyte, *i.e.*, for constant r_c and r_a , ϵ_s may be varied by varying the solvent to which the ions are transferred. The plot of ΔG_t° against ϵ_s^{-1} should then be a straight line. Feakins and French³ examined this point exhaustively for transfers of hydrochloric acid from water to aqueous-organic solvent mixtures and showed that this test failed hopelessly. A correlation, particularly good for methanol-water mixtures over a wide range of concentration, was shown to exist between ΔE_t° and $\log \phi_w$, where ϕ_w is the volume fraction of water in the mixed solvent. This was rationalised by assuming specific solvation of the ions by water molecules. The "solvation number" required (~ 2) is suspiciously low, and it is certain that this theory is too naive.

Secondly, the effect of variations in the ionic radii for transfers from water to a particular mixed solvent, *i.e.*, for constant ϵ_s , may be studied. The radii used, which are Pauling's,⁵ are in Table 2.

TABLE 2.

Ion	Ionic radii (Å).					
	Li ⁺	Na ⁺	K ⁺	Cl ⁻	Br ⁻	I ⁻
r	0.607	0.958	1.331	1.806	1.951	2.168

³ Feakins and French, *J.*, 1957, 2581.

⁴ Åkerlöf, *J. Amer. Chem. Soc.*, 1930, 52, 2353.

⁵ Pauling, "The Nature of the Chemical Bond," Oxford Univ. Press, London, 3rd edn., p. 519.

If ΔG_t° is plotted against r_a^{-1} for the transfers of the hydrogen halides from water to (a) 10% and (b) 43.12% methanol mixtures, a straight line results in the first case from which the mean deviation of the points is negligibly small. In the second case, the deviations from linearity (18 cal.) are somewhat greater than the experimental error and a curve drawn through the three points would be slightly concave towards the axis of r_a^{-1} . For the moment we shall ignore any deviation from linearity in this plot.

The slopes of the lines are (a) 1.36×10^3 cal. Å and (b) 7.50×10^3 cal. Å, respectively. The slopes predicted by equation (2) are (a) 1.25×10^2 cal. Å and (b) 6.69×10^2 cal. Å, which in both cases are incorrect by factors of 10. Let us, however, tentatively retain the view that the free energy of transfer of an ion is inversely proportional to its crystallographic radius. This enables us to write, for the hydrogen halides:

$$\Delta G_t^\circ = \Delta G_t^\circ(\text{H}^+) + ar_a^{-1}, \quad (3)$$

where a is a constant and $\Delta G_t^\circ(\text{H}^+)$ is the free energy of transfer of the proton. From the graphs, the values of $\Delta G_t^\circ(\text{H}^+)$ are for the respective transfers (a) -570 cal. and (b) -3430 cal., signifying that both mixtures are more basic than water. The free energies of transfer of the chloride ion are, by difference, (a) $+750$ cal. and (b) $+4130$ cal.

The plots of ΔG_t° against r_c^{-1} for the alkali chlorides are also approximately rectilinear, with mean deviations from the best straight lines of (a) 7 cal. and (b) 21 cal., respectively equal to and greater than the experimental error. However, the range of r^{-1} covered is now much greater than before. The slopes of the two lines are (a) -1.64×10^2 cal. Å and (b) -8.30×10^2 cal. Å. These are opposite in sign to the slopes predicted from equation (2).

We have seen, from the first plots, that the proton is in a lower free-energy state in the mixed solvents than in water. Suppose that this is true also for all other cations, and that they are more stable, in the mixed solvents than in water itself, to an extent, for a given charge, inversely proportional to their radii.

We may then write, for the alkali chlorides,

$$\Delta G_t^\circ = \Delta G_t^\circ(\text{Cl}^-) - br_c^{-1}. \quad (4)$$

Extrapolation of the two lines to $r_c^{-1} = 0$ gives values of $\Delta G_t^\circ(\text{Cl}^-)$ of (a) 615 cal. and (b) 2910 cal., respectively. These agree sufficiently well with the results from the longer "anion" extrapolations to suggest that a correct semi-quantitative description of these systems has been found, although it is not claimed that the correct dependence of ΔG_t° upon r has been established.

The mean values of $\Delta G_t^\circ(\text{Cl}^-)$ are (a) $+680$ cal. and (b) $+3530$ cal. and these have been used to separate the ΔG_t° values for pairs of ions into the individual ionic values shown in Table 3.

TABLE 3.

Ionic molar free energies of transfer from water, ΔG_t° (cal.).

	H ⁺	Li ⁺	Na ⁺	K ⁺	Cl ⁻	Br ⁻	I ⁻
To 10% methanol ...	-500	-340	-230	-200	+680	+630	+560
To 43.12% methanol	-2800	-2000	-1400	-1200	+3500	+3200	+2800

Slansky⁶ has determined the heats of solution of a number of alkali halides and of hydrogen chloride in water and methanol, and their mixtures with each other, and these can be used to calculate enthalpies and entropies of transfer in the two cases of interest. These are shown in Table 1. There are some instances of non-additivity in Slansky's figures, and the values of ΔH_t° quoted for the halogen acids are obtained from those for hydrochloric acid and means of the values for the sodium and potassium halides. No

⁶ Slansky, *J. Amer. Chem. Soc.*, 1940, **62**, 2430.

obvious basis, similar to that used above, exists for the separation of the heat and the entropy data into individual ionic values.

If any further proof of the inadequacy of Born's approach were required, these figures supply it. From equation (2), and equation (5) derived from it,

$$\Delta S = \frac{Ne^2}{2} \left[\frac{1}{\epsilon_s^2} \left(\frac{d\epsilon_s}{dT} \right) - \frac{1}{\epsilon_w^2} \left(\frac{d\epsilon_w}{dT} \right) \right] \left[\frac{1}{r_c} + \frac{1}{r_a} \right], \quad (5)$$

values of ΔG_t° , ΔH_t° , and $-T\Delta S_t^\circ$ may be calculated. With the transfer of lithium chloride from water to 10% methanol as an example, these are, respectively, +275, -450, and +725 cal. and may be contrasted with the experimental values in Table 1.

It is convenient to summarise the main conclusions which can be reached so far.

(1) The Born approach fails every quantitative or even semi-quantitative test, and is useless as a guide to the thermodynamic properties of the ions in these systems.

If the above separation into individual ionic values is accepted, we further conclude:

(2) The cations are in lower free-energy states in the methanol-water mixtures than in water.

(3) Transfers of the halide ions from water to these media are, by contrast, disfavoured.

(4) The free energy of transfer of all the anions studied is greater numerically than that of any of the cations, despite the smaller radii of the latter.

Let us assume that there are two main effects contributing to the free energy of an ion. First, the ion affects the structure of the solvent. It may create new centrosymmetric structures around itself, make, break, strengthen, or weaken hydrogen bonds. Secondly, it has a potential energy due to the interaction of its own charge with the complex distributions of charge on the solvent molecules, which includes any attractive covalent interaction with nearest-neighbour water molecules.

Insofar as the first effect is analogous to a freezing or melting process for which $\Delta G = 0$, its contribution to the free energy of solvation of the ion may well be small, though large structural contributions to the enthalpy and entropy of transfer are not precluded.

There is some evidence to support this assumption. Up to a concentration of 90% methanol, the free energies of transfer of lithium, sodium, and potassium chloride and of hydrochloric acid, vary monotonically with solvent composition.⁴ (Between 90% and 100% methanol it is possible that the free energies of transfer of sodium and potassium chlorides pass through small maxima. Unfortunately there are not sufficient reliable data to establish this.) By contrast, the enthalpies of transfer of all these electrolytes pass through pronounced maxima in the region of 20–30% methanol.⁶ This region appears to be a critical one structurally,⁷ for the heats and excess entropies of mixing of the two components show minima; the viscosities of the mixtures and the Walden product of the proton show maxima. The enthalpy of transfer therefore appears to be influenced by structural factors, but not the free energy, which is therefore assumed to be dominated by the second of the two classes of interaction mentioned above.

There are then three relevant properties. First, the detailed charge distributions in the solvent molecules. The inductive effect of the methyl group should both increase the electron density on the oxygen atom and leave the hydroxyl-hydrogen atom less positively charged in methanol than in water. The methanol molecule is thus more "basic" and less "acidic" than the water molecule. Secondly, the dipole moment of each molecule. The gas phase values of these, which may be modified in an associated liquid, are 1.69 D for methanol and 1.84 D for water.⁸ Thirdly, the dielectric constants of the two solvents and their mixtures with each other, which vary monotonically from 78.5 for water to 31.5 for methanol.⁹

⁷ Brown and Ives, *J.*, 1962, 1608.

⁸ Smith, "Electric Dipole Moments," Butterworths Scientific Publns., London, 1955, p. 86.

⁹ Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Rheinhold Publishing Corp., New York, 3rd edn., p. 161.

Consider the solvation of an alkali-metal cation. Here, the solvent molecule in a first sheath round the ion are probably orientated with their oxygen atoms pointing towards the ion, possibly with oxygen lone-pair orbitals overlapping the acceptor orbitals (*s*, *p*, and *d*, if available) of the ion. If we make no distinction between ionic and covalent bonding, the strength of the interaction between ion and solvent molecule will depend to a first approximation on the electron density on the oxygen atom of the solvent molecule, and will be stronger for methanol than for water.

It is also possible that a methanol molecule can cause some charge displacement in a water molecule to which it is bonded, making it in turn more basic and less acidic. If a co-operative theory of hydrogen bonding in liquid water¹⁰ is correct, this effect could well be relayed over several molecular diameters. It is, therefore, unnecessary to speculate about the composition of the first solvation sheath in a methanol-water mixture: the presence in it of either type of molecule will lower the energy of the ion with respect to its value in pure water. Similar arguments apply to the solvation of the proton, except that the primary solvated species are $\text{CH}_3\cdot\text{OH}_2^+$ and H_3O^+ .

A halide ion will probably be surrounded by solvent molecules so orientated that a hydroxyl-hydrogen atom is immediately adjacent to the ion and the ionic, hydrogen, and oxygen nuclei are co-linear, as in a hydrogen bond of optimum stability. The strength of the attraction between the ion and the solvent molecules will be dominated by the coulombic force between the charge on the ion and the charges on the hydroxyl-hydrogen atoms and, as far as the primary solvation is concerned, an anion will be in a lower free-energy state in water than in the mixed solvents. The centroids of charge of the relevant sign on the solvent molecule probably approach the "surface" of the ion closely, so that the primary solvation energy of ions of both signs is approximately proportional to the electrostatic fields at their "surfaces" or inversely proportional to the ionic radii.

The importance of the actual charge distribution in the molecule, rather than its dipole moment, in determining the primary solvation energy, has been emphasised by Hudson and Saville,¹¹ particularly, and by Verwey¹² and Buckingham.¹³ The "acidic" and "basic" functions of the molecule are thought to be of dominant importance in the solvation of anions and cations, respectively.

In second and subsequent shells round an ion, the ionic field may at first be strong enough to cause dielectric saturation. Here an ion and a solvent molecule are probably far enough apart for the detailed charge distribution of the solvent molecule to be ignored, and their interaction calculated as that between a point charge and a structureless dipole.

Further out, the ionic field becomes sufficiently low for any further contribution to the free energy of solvation to be computed by Born charging. The effect of the last two contributions to the total free energy is in the same sense for anions as for cations, opposing the effect of the primary solvation in the case of cations and reinforcing it in the case of anions. If we assume the effects of primary solvation to be dominant, the net result will be small negative free energies of transfer in the case of cations and large positive free energies of transfer in the case of anions, as observed.

This interpretation differs at many points from that put forward by Grunwald, Baughman, and Kohnstam, in their important paper,² to explain the analogous effects in dioxan-water mixtures. They assume that, in general, anions are specifically solvated by water molecules, but that partial dioxanation, at least, of cations occurs. The solvent molecules are considered to be firmly bound to the ions, and the free energy of solvation is computed as the reduction in the total free energy of the solvent by loss of solvent molecules to the ions to form "ion complexes." These assumptions are sufficient to explain the highly characteristic behaviour of cations and anions.

¹⁰ Frank and Wen-Yang Wen, *Discuss. Faraday Soc.*, 1957, **24**, 133.

¹¹ Hudson and Saville, *J.*, 1955, 4114.

¹² Verwey, *Rec. Trav. chim.*, 1942, **61**, 127.

¹³ Buckingham, *Discuss. Faraday Soc.*, 1957, **24**, 133.

This effect is ignored in our treatment, but may well be significant. However, if Grunwald, Baughman, and Kohnstam's treatment is to apply over the whole range of dioxan-water compositions, it is necessary to modify it by the introduction of solvation numbers for the various ions which vary with solvent composition. This must involve some consideration of the difference in interaction energy between the ions and the two types of solvent molecule, as in the present treatment.

Neither interpretation leads to *a priori* calculations of free energies of transfer, and as no judgment between them seems possible at present, they will not be further compared.

Other Solvents.—Table 4 displays data for transfers from water to 60% and 90% methanol solutions and to pure methanol. For the last transfer, a graph of ΔG_t° against r_a^{-1} for the hydrogen halides would be so far from linearity that no extrapolation to $r_a^{-1} = 0$ could reasonably be made.

TABLE 4.

Molar free energies of transfer from water, ΔG_t° (cal.).

	HCl	HBr	HI	LiCl	NaCl	KCl
To 60% methanol	1070 *	—	—	2240 †	3030 †	3420 †
„ 90% „	2750 *	—	—	3980 †	5340 †	6540 †
„ 100% „	5650 ‡	4990 §	3200 ¶	4800	5700 **	6600 **

Based on e.m.f. data from various sources. * Ref. 14. † Ref. 4. ‡ Ref. 15. § Ref. 1. ¶ Ref. 17. || Ref. 18. ** Ref. 19.

The explanation must lie in the “ non-electrolyte ” part of the interaction of the ions with the solvents. The free energies of transfer of inert gases from water to methanol are shown in Table 5. The big difference in behaviour between neon and argon compared with that between helium and neon will be noted. A similar effect may account for differences between the three halide ions.

TABLE 5.

Molar free energies of transfer of inert gases from water to methanol, ΔG_t° (cal.).

He *	Ne *	Ar *	Rn †
790	840	1220	1800

Based on solubility data from: * ref. 20, † ref. 21 (extrapolated).

It will be noted that the free energy of transfer of the helium atom is small compared with that of any of the electrolytes studied. As most simple cations are smaller than helium, their free energies of transfer will contain only small contributions from “ non-electrolyte ” effects, and extrapolations based on cation behaviour may be more reliable than those based on the behaviour of anions.

Table 6 displays values of the free energies of transfer of single ions, calculated on the basis of the data for the alkali chlorides only, over the whole range of methanol-water compositions. The variation of free energy of transfer with solvent composition is not monotonic in the region of 90–100% methanol. Some “ uncompensated ” structural effect clearly becomes important in this region, which is also a critical one structurally: ⁷ the data for the cations are consistent with this being an entropic effect due to increased structure-making by the ions as the water content of the mixture decreases. It is known

¹⁴ Oiwa, *J. Phys. Chem.*, 1956, **60**, 654.

¹⁵ Koskikallio, *Suomen Kem.*, 1957, **30 B**, 38, 43, 111.

¹⁶ Kanning and Campbell, *J. Amer. Chem. Soc.*, 1942, **64**, 517.

¹⁷ Izmailov and Ivanova, *Zhur. fiz. Khim.*, 1955, **29**, 1614.

¹⁸ Izmailov, *Russ. J. Phys. Chem.*, 1960, **34**, 1142 (English translation).

¹⁹ Gladden and Fanning, *J. Phys. Chem.*, 1961, **65**, 76.

²⁰ Seidell, “ Solubilities of Inorganic and Metal Organic Compounds,” Vol. I, Van Nostrand, New York, 3rd edn., pp. 1, 601, 604, 1336.

²¹ Internat. Critical Tables, Vol. III, McGraw-Hill, 1st edn., p. 263; ref. 20, p. 1426.

TABLE 6.

Ionic molar free energies of transfer from water, calculated from the " anion extrapolations," ΔG_t° (cal.).

To methanol (%)	10	43.12	60	90	100
H ⁺	-435	-2200	-3300	-5700	-2500
Li ⁺	-275	-1400	-2200	-4500	-3100
Na ⁺	-160	-800	-1400	-3100	-2200
K ⁺	-130	-600	-1000	-1900	-1100
Cl ⁻	+615	+2900	+4400	+8500	+7900

that the structure-making tendencies of ions increase on passing from water to methanol.²² The data are not very reliable, but there seems little doubt about the large effect for the proton. Methanol is a stronger base than water, but a weaker one than a 90% methanol-water mixture. A similar effect is shown by Hammett's acidity function.²³

The measurements of Grunwald, Baughman, and Kohnstam² may be explained by assuming the dioxan molecule to be more " basic " than the water molecule and to enhance the " basicity " of water molecules to which it is bonded. It has no " acidic " function, but will reduce the " acidity " of water molecules to which it is bonded.

Acidity Functions.—Hammett's acidity function is based on the equilibrium:



B is an organic base. In aqueous mixtures of acetone, ethanol, dioxan,²⁴ and methanol,²³ this equilibrium lies further to the left than in pure water except where the concentration of the organic component is high (above ~90% by weight). By this criterion the former mixtures are more basic than water. These results mean that the quantity

$$\sum \Delta G_t^\circ = \Delta G_t^\circ(H^+) - [\Delta G_t^\circ(BH^+) - \Delta G_t^\circ(B)] \quad (7)$$

is negative for transfers from water to these mixtures.

The square-bracketed quantity in equation (7) may be taken as the free energy of transfer of a large cation, approximately corrected for its " non-electrolyte " interactions. According to the arguments outlined above, this quantity should be in the same sense as $\Delta G_t^\circ(H^+)$, and thus, in general,

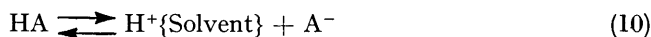
$$\sum \Delta G_t^\circ > \Delta G_t^\circ(H^+). \quad (8)$$

The acidity function will thus tend to underestimate the basicity of the medium. For it to be qualitatively correct:

$$\Delta G_t^\circ(BH^+) - \Delta G_t^\circ(B) \ll \Delta G_t^\circ(H^+). \quad (9)$$

This should in general be true because the electrostatic field around the BH⁺ ion should be smaller than that due to a proton. The apparently lower basicities, relative to water, of pure or slightly aqueous alcohols, dioxan, and acetone, as judged by the study of equilibria such as (6), could however be due to a failure of inequality (9) rather than to intrinsically lower basicities.

The position of equilibrium in the reaction



is also used as a criterion of basicity. In alcohols, acetone, dioxan, and all their aqueous

²² Parsons, " Handbook of Electrochemical Constants," Butterworths Scientific Publns., London, 1959, pp. 76, 77.

²³ de Ligny, Loriaux, and Ruiter, *Rec. Trav. chim.*, 1961, **80**, 725; de Ligny, *ibid.*, 1960, **79**, 731; Salomaa, *Acta Chem. Scand.*, 1957, **11**, 125.

²⁴ Braude, *J.*, 1948, 1971; Braude and Stern, *ibid.*, 1976.

mixtures this equilibrium lies further to the left than in water, and by this criterion these media are less basic than water. In our terminology the quantity

$$\sum_1 \Delta G_t^\circ = \Delta G_t^\circ(\text{H}^+) + [\Delta G_t^\circ(\text{A}^-) - \Delta G_t^\circ(\text{HA})] \quad (11)$$

is positive for transfers from water to these solvents.

The square-bracketed quantity in equation (11) may be taken as the free energy of transfer of an anion, approximately corrected for its "non-electrolyte" interactions. A^- is a weak acid anion and its interaction with the hydrogen atoms of solvent molecules must be strong. It is probable that it will invariably have a free energy of transfer numerically greater than, though opposite in sign to, that of any cation, including the proton. Thus $\sum_1 \Delta G_t^\circ$ of equation (11) will always be positive for transfers from water to these other media, even though $\Delta G_t^\circ(\text{H}^+)$ may be negative. The study of equilibria such as (10) is therefore unlikely to be even a useful qualitative guide to the relative basicities of these solvents.

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