Theoretical Calculations of Thermodynamic Functions of Solvation of Ions

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Abstract: Thermodynamic functions have been calculated for the solvation of simple ions in water. Calculations are based upon modifications of the Born equation for the electrostatic free-energy change of an ion passing from a vacuum to a medium of specified dielectric constant. The dielectric saturation of solvent molecules in the vicinity of an ion is considered. The consistency of the results confirm that calculations for the free-energy change in such systems should incorporate a treatment of a field-dependent dielectric constant. It is suggested that the ionic crystallographic radius is only suitable for calculations involving alkali metal ions. For multivalent ions, radii are assigned on the basis of a partial covalent contribution to the bonding between the ions and the solvating molecules adjacent to the ion. In all cases the radii assigned are in keeping with experimental observations on ionic hydration.

Attempts to calculate the free energy of solvation of an ion in a given medium have been only partially successful. Early treatments were based upon direct application of the Born equation.[1] The Born theory gives the change in electrostatic free energy $\Delta G^\circ_{\text{el}}$, when a charge q is transferred from a conducting sphere of radius a in a vacuum to a sphere of equal radius in a medium of dielectric constant D, as

$$\Delta G^\circ_{\text{el}} = \frac{-q^2}{2a}\left(1 - \frac{1}{D}\right) \qquad (1)$$

For an ion of charge Ze and radius r in water at 25°, the values of $\Delta G^\circ_{\text{el}}$ predicted by eq 1 are too high. Correlation between experiment and theory is obtained mainly in two ways.

(a) Using ionic radii greater than the ionic crystallographic radii. Thus Voet,[2] Latimer, Pitzer, and Slansky,[3] Hush,[4] Grahame,[5] and Powell and Latimer[6] found agreement with experiment by the addition of constant amounts to the ionic radii.

(b) Incorporating some theory of dielectric saturation. In this respect the variation of the dielectric constant as a function of field strength is invoked to produce results more in keeping with experimental observations. Webb[7] and Ingold[8] used Debye's[9] early theory of dielectric saturation in their calculations. Debye, however, neglected the mutual interaction of neighboring molecules, and his theory, therefore, was not applicable to associated liquids such as water.

More recent treatments include those of Laidler and Pegis[10] and of Glueckauf.[11] Laidler and Pegis have used a modification of the Booth theory[12] of saturation as well as modified radii. It was their contention that the relatively consistent set of results so obtained justified the modifications. Glueckauf has used Booth's theory and incorporated a space parameter into the equation. The dielectric constant is taken as unity for a distance from the surface of the ion equal to the space parameter. This parameter was chosen so that the function reproduced correctly the enthalpies of solvation of the alkali ions in water. It has since been shown[13] that Booth's theory does not adequately describe the change of dielectric displacement with field strength.

In the vicinity of the surface of an ion, the electrostatic potential gradient is of the order of 10^6 v cm^{-1}. Polarization and orientation of the solvent molecules in the neighborhood of the ion occurs with consequential lowering of the dielectric constant below the normal bulk value. It is considered that any theory on ionic solvation must take cognizance of this field dependence of dielectric constant.

Here, we calculate free energies of solvation of a number of ions in water at 25 and 80° and attempt to allow for the effects of dielectric saturation. From the temperature dependence of the free-energy change, the enthalpy and entropy changes are calculated. Modification to the radius parameter appearing in the Born expression has been made with the intention to represent more closely the real situation. Finally, nonelectrostatic free-energy terms have been included to account for the surface free energy in making a hole in the liquid and for the volume change when 1 mole of ions is transferred from the gas to the liquid phase.

If successful, a theory of this nature may then be used to evaluate solvation energies of ions in any solvent for which the appropriate physical parameters are known.

Mathematical Expression for Saturation of the Dielectric

An extension of the theory of Harris and Alder[14] has been used to describe mathematically the saturation of the dielectric. Harris and Alder have improved the original theories of Kirkwood[15] and of

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(1) M. Born, *Z. Physik*, **1**, 45 (1920).
(2) A. Voet, *Trans. Faraday Soc.*, **32**, 1301 (1936).
(3) W. M. Latimer, K. S. Pitzer, and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).
(4) N. S. Hush, *Australian J. Sci. Res.*, **1**, 480 (1948).
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(6) R. E. Powell and W. M. Latimer, *ibid.*, **19**, 1139 (1951).
(7) T. J. Webb, *J. Am. Chem. Soc.*, **48**, 2589 (1926).
(8) C. K. Ingold, *J. Chem. Soc.*, 2179 (1931).
(9) P. Debye, *Handb. Radiol.*, **6**, 618, 680 (1925).
(10) K. J. Laidler and C. Pegis, *Proc. Roy. Soc.* (London), **A241**, 80 (1957).
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(12) F. Booth, *J. Chem. Phys.*, **19**, 391, 1327, 1615 (1951).
(13) A. D. Buckingham, *ibid.*, **25**, 428 (1956).
(14) F. E. Harris and B. J. Alder, *ibid.*, **21**, 1031 (1953).
(15) J. G. Kirkwood, *ibid.*, **7**, 911 (1939).

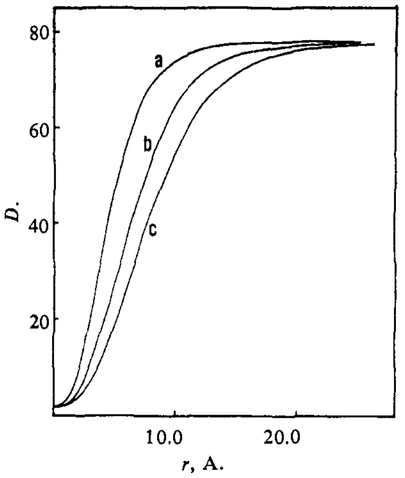

Figure 1. Variation of dielectric constant of water with distance from center of ions of charge Z: (a) $Z = 1$, (b) $Z = 2$, (c) $Z = 3$.

Fröhlich[16] for the static dielectric constant of polar substances. By a more precise evaluation of the distortion polarization term, the dielectric constants of pure water and of heavy water were calculated to within 2% of the experimental values over a wide temperature range. The static dielectric constant of a polar substance was expressed as

$$D = \frac{4\pi N_0}{3}\alpha(D + 2) + \frac{4\pi N_0}{3}\frac{\mu^2}{3kT}g\frac{9D}{(2D + 1)} + 1 \tag{2}$$

Here D is the static dielectric constant, N_0 is the number of molecules per cubic centimeter, α is the molecular polarizability, and k and T are the Boltzmann constant and absolute temperature, respectively. μ and g are dipole moment and correlation terms, respectively.

The dipole moment, μ, of a solvent molecule in the bulk liquid differs from the moment, μ_0, in the gas phase owing to induction of an additional moment by the dipole field of its neighbors. Because of this polarization, μ is greater than μ_0. Difficulty arises in attempting to calculate μ exactly and recourse is made to the approximate relationship derived by Onsager.[17] If one assumes the Onsager reaction field to be valid, then

$$\mu = \mu_0\frac{(n^2 + 2)}{3}\frac{(2D + 1)}{(2D + n^2)} \tag{3}$$

n being the refractive index of the solvent at visible frequencies.

The factor g represents the effect of correlation due to intermolecular interactions. If the orientation of one molecule is fixed and the neighbors of this fixed molecule are divided into shells, then [18]

$$g = (1 + \sum_{i=1}^{\infty} Z_i\langle\cos\gamma_i\rangle_{\text{av}}) \tag{4}$$

where Z_i is the number of particles in the ith shell and is obtainable from X-ray data on the liquid. γ_i is the angle between the molecular axis of a molecule in the ith shell and that of the fixed central molecule. $\langle\cos\gamma_i\rangle_{\text{av}}$ is an average over all configurations of both molecules. This correlation parameter is then a useful index to the degree of hindered rotation in a liquid.

Because of random thermal rotations, a liquid ordinarily has an average moment of zero. If it is placed in an orienting field E, however, it tends to align itself with the field so that the average component of the dipole moment parallel to the field is $\bar{\mu}$. Classically, if the system is in thermal equilibrium

$$\bar{\mu} = \mu\mathrm{L}(x)$$

where $\mathrm{L}(x)$ is the Langevin function of the argument x and is given by $\mathrm{L}(x) = \coth x - (1/x)$. Therefore, in order to express the dielectric constant as a function of field strength, we have embodied the Langevin function into the orientation polarization term in the derivation of eq 2. For a spherically symmetrical field of magnitude E, (2) becomes

$$D = \frac{4\pi N_0}{3}\alpha(D + 2) + 4\pi N_0 g\mu\mathrm{L}(x)\frac{1}{E}\times \frac{9D}{(D + 2)(2D + 1)} + 1 \tag{5}$$

where

$$\mathrm{L}(x) = \mathrm{L}\left[\frac{\mu E}{kT}\frac{(D + 2)}{3}\right]$$

in which $E(D + 2)/3$ is the internal field.[14] By expressing the field strength in terms of r, the distance from the center of the ion to the point of application of the field, then

$$E = q/Dr \tag{6}$$

Substitution of (6) in (5) and in the Langevin function then gives the implicit function used in this paper to describe the dielectric constant as a function of field strength. Equation 5 reduces to (2) for low fields for which $\mathrm{L}(x) = x/3$.

Figure 1 shows the dielectric constant D as a function of r. In practice the rigorous evaluation of g from models for water is difficult. For this reason we have chosen g such that the bulk dielectric constant for water is obtained for low fields as represented by (2). For the temperature range with which we are concerned there is little deviation from the original results of Harris and Alder.

The final form of Figure 1, though similar to the results of Padova[19a] and Hasted and Ritson,[19b] suggests that the effects of dielectric saturation extend futher from the central ion.

Development of an Expression for the Electrostatic Free Energy of Solvation

If we assume an ion of charge q to be a conducting sphere or a uniformly charged nonconducting sphere of radius r_g in the gas phase, there is an intrinsic standard free energy $G°(g)$, associated with it by virtue of its electrostatic charge. This energy is defined as

$$G°(\mathrm{g}) = \int_0^{Ze}\int_{\infty}^{r_g}\frac{q}{r^2}\,\mathrm{d}r\mathrm{d}q \tag{7}$$

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[16] H. Fröhlich, "Theory of Dielectrics," Oxford University Press, London, 1949.

[17] L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).

[18] J. A. Pople, *Proc. Roy. Soc.* (London), **A205**, 163 (1951).

[19] (a) J. Padova, *J. Chem. Phys.*, **39**, 1552 (1963); (b) J. B. Hasted and D. M. Ritson, *ibid.*, **16**, 11 (1948).

where Z is the charge magnitude and e is the electronic charge.

In a continuous medium of variable dielectric constant the standard partial molar electrostatic free energy, $\bar{G}°(\mathrm{l})$, of this ion is a function of the variable dielectric constant. Thus

$$\bar{G}°(\mathrm{l}) = \int_0^{Ze} \int_\infty^{r_s} \frac{q}{D(r,q)r^2}\, \mathrm{d}r\mathrm{d}q \qquad (8)$$

where the limits of integration over dr in (7) and (8) are taken from infinity to the surface of the ion in its respective phase. Therefore, r_g refers to the ionic radius in the gas phase and r_s to the ionic radius in solution.

The electrostatic standard free energy of solvation, $\Delta G°_{\mathrm{el}}$, is then given as

$$\Delta G°_{\mathrm{el}} = \bar{G}°(\mathrm{l}) - G°(\mathrm{g}) = \int_0^{Ze} \int_\infty^{r_s} \frac{q}{D(r,q)r^2}\, \mathrm{d}r\mathrm{d}q - \int_0^{Ze} \int_\infty^{r_g} \frac{q}{r^2}\, \mathrm{d}r\mathrm{d}q \qquad (9)$$

which reduces to

$$\Delta G°_{\mathrm{el}} = \int_0^{Ze} \int_\infty^{r_s} \frac{q}{D(r,q)r^2}\, \mathrm{d}r\mathrm{d}q - \frac{Z^2e^2}{2r_g} \qquad (10)$$

All that remains now is to include the nonelectrostatic free-energy terms. Before this is done it is convenient to discuss the choice of the most realistic values of r_g and r_s for each ion.

Because of the great range of ionic potentials involved in the calculation of solvation energies for even such simple group A type ions as Na^+, K^+, Ca^{2+}, Al^{3+} etc., it is obvious that the ordinary ionic crystallographic radii of Goldschmidt[20] and Pauling[21a] are unlikely to be suitable for all ions especially when it is recognized[21b] that there is a considerable covalent contribution to the solvation of the more highly charged ions.

Laidler[22] has shown that the univalent radii of Pauling are suitable for the calculation of thermodynamic properties of ions. These univalent radii are larger than the ionic radii of multivalent ions but equal to the ionic radii for univalent ions. Laidler and Pegis[10] have also increased the ionic radii of Goldschmidt by 25% in the calculation of partial molal volumes and hydration energies. It must be emphasized as pointed out by Laidler and Pegis that any such increase in radius is only relevant to the calculation of $\bar{G}°(\mathrm{l})$.

Stern and Amis[23] have considered the question of ion size and discuss a number of methods for determination of the radii of ions, the results varying appreciably from method to method. For the radii of solvated ions they conclude that "the term radius is virtually meaningless" since the ions may possess solvation sheaths of water molecules bound "permanently" to the ion to give a distinct molecular species.

Taube,[24] using O^{18} isotopic fractionation techniques, supports this idea of a first-sphere hydration sheath. In this respect Al^{3+} and Mg^{2+} show "first-sphere hydration" while Na^+, K^+, and Cs^+ do not. These conclusions are supported by those of Samoilov[25] from self-diffusion studies of water. Samoilov concluded that K^+, Cs^+, Br^-, and I^- are all "unhydrated" in aqueous solution while Mg^{2+} and Ca^{2+} do have hydration sheaths associated with them. Using O^{17}, Taube, *et al.*,[26] have also shown that a separate nmr peak due to the hydrated ion is observed for Be^{2+}, Al^{3+}, and Ga^{3+}. This requires that the lifetime of the hydrated species is of the order of 10^{-4} sec or longer. More recent measurements on the nmr spectra of aqueous salt solutions by Swift and Sayre[27] allow primary hydration numbers to be evaluated for alkaline earth metal ions. Covalent forces are considered as plausible in bonding between Be^{2+} and the hydrating water molecules.

With this experimental evidence as basis we have assigned ionic crystallographic radii to the alkali metal ions Na^+, K^+, Rb^+, and Cs^+ in solution. Measured electron densities in NaCl crystals have shown[28] that a radius of 1.17 A is to be attributed to the Na^+ ion viewed as a sphere. Similarly, all alkali metal ion radii taken here are the set derived from electron-density measurements.

We have found that a self-consistent set of radii for the multivalent ions in solution are obtained by considering the effective nuclear charges on the ions. Within an isoelectronic sequence of ions the radius of the ion in solution is taken as varying directly as the effective nuclear charge. Thus $r_s = CZ_{\mathrm{eff}}$ for multivalent ions, where $Z_{\mathrm{eff}} = (Z_n - S)$, for Z_n the true nuclear charge and S a screening constant. The constant of proportionality is fixed using the data for the alkali metal ions for which the ionic radii are used. Screening constants have been examined from three different sources[29–31] and give the same values of the multivalent radii to within 1 or 2%. The radii for multivalent ions in solution as determined using Slater's[29] screening constants are given in Table I. It is interesting to observe that remarkable agreement exists between these calculated radii for the divalent ions and Pauling's covalent radii in hydride compounds.[32]

The need to assign a radius to the gaseous ion has been obviated by assigning a complete energy term to the second term in eq 10. We have identified the term $Z^2e^2/2r_g$ with the sum of the standard free energies of ionization of the ion. Hush[4] gives the method of evaluation of these standard free energies of ionization for a series of ions using basic thermodynamic functions. Standard ionization enthalpies at 0°[33] together with standard ionization free energies are given in Table I. Values of r_g calculated using our value of $G°(\mathrm{g})$ in the expression $G°(\mathrm{g}) = Z^2e^2/2r_g$ are also tabulated. Stokes[34] has calculated the energy term for the gaseous ion by using a van der Waal's radius. These radii

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(21) (a) L. Pauling, "The Nature of the Chemical Bond," Vol. 3, Cornell University Press, Ithaca, N. Y., 1960, p 514; (b) *J. Chem. Soc.*, 1461 (1948).

(22) K. J. Laidler, *Can. J. Chem.*, **34**, 1107 (1956)

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(30) L. Pauling, *Proc. Roy. Soc.* (London), **A114**, 181 (1927).

(31) L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

(32) Reference 20, p 256.

(33) B. Lakatos, J. Bohus, and Gy. Medgyesi, *Acta Chem. Hung.*, **20**, 1 (1959).

(34) R. H. Stokes, *J. Am. Chem. Soc.*, **86**, 979 (1964).

Table I. Summary of Data for the Change in Standard Free Energy of Solvation of Ions in Water at 25°[a]

Ion	r_s, A	Sum of ionization enthalpies	Ionization free energies at 298.16°K	r_g, A	$\bar{G}°(l)$	$\Delta G°_h$	$\Delta G°_v$	Σ(col 6–8)	$-\Delta G°_{sol}$		$-\Delta G°_{sol}$ (H^+)	Diff %, $\Delta G°_{sol}(H^+)$ and −260.5
									Calcd	Exptl		
Na^+	1.17	118.49	119.32	1.391	10.25	8.25	1.89	20.39	98.9	98.2	261.2	−0.27
K^+	1.49	100.07	100.90	1.645	5.29	13.36	1.89	20.54	80.6	80.4	260.3	+0.08
Rb^+	1.63	96.31	97.14	1.709	4.16	16.01	1.89	22.06	75.1	75.5	260.1	+0.15
Cs^+	1.86	89.78	90.61	1.832	2.95	20.83	1.89	25.67	64.9	67.8	257.6	+1.11
Mg^{2+}	1.34	522.91	524.41	1.266	51.11	10.84	1.89	63.84	460.6	455.5	263.1	−0.61
Ca^{2+}	1.68	414.63	416.13	1.596	27.81	16.98	1.89	46.68	369.5	380.8	254.9	+2.15
Sr^{2+}	1.80	385.60	387.10	1.715	23.01	19.50	1.89	44.40	342.7	345.9	258.9	+0.61
Ba^{2+}	2.06	351.28	352.78	1.882	15.90	25.52	1.89	43.31	309.5	315.1	257.7	+1.07
Al^{3+}	1.51	1227.98	1230.07	1.215	116.41	13.73	1.89	132.03	1098.0	1103.3	258.7	+0.69
Sc^{3+}	1.87	1019.34	1021.43	1.463	66.31	21.07	1.89	89.27	932.2	929.3	261.5	−0.38
Y^{3+}	1.98	906.34	908.43	1.645	56.76	23.60	1.89	82.25	826.2	859.5	249.5	+1.26
La^{3+}	2.26	862.75	864.84	1.728	39.48	30.76	1.89	72.13	792.7	779	265.1	−1.77

[a] All thermodynamic quantities are given in kcal mole^{-1}.

being much larger than the corresponding ionic crystallographic radii are considered to apply to the specific case of gas-phase ions where the outer electron distribution may expand. Our calculated values for r_g are similar to those of Stokes.

Nonelectrostatic Free-Energy Terms

While it is impossible to include all the nonelectrostatic free-energy terms contributing to the free-energy change of solvation, the two major terms may be evaluated with some assurance. The first of these accounts for the change in volume of the ionic gas on its dissolution in the solvent to form a 1 *M* solution. At 25°, 1 mole of gas has a volume of 24.47 l. at 1 atm pressure. On forming a 1 *M* solution, the standard free energy of the system is increased for the isothermal volume change by

$$\Delta G°_v = -RT \ln \frac{1}{24.47} = 1.89 \text{ kcal mole}^{-1}$$

Similarly at 80°, the increase in free energy is 2.36 kcal mole^{-1}. This term is constant for all ions at any one temperature.

The second term is the free energy of formation in the solvent of the hole occupied by the ion. Following Drakin and Mikhailov[35,36] we calculate this energy contribution as the work of creating a liquid surface equal to the surface of a sphere of radius r_s. The free energy in making this hole is then $\Delta G°_h = 4\pi r_s^2\sigma$, where σ is the free energy per square centimeter of liquid surface.

At constant pressure σ is related to the total surface energy E_s by the equation

$$E_s = \sigma - T\left(\frac{\partial \sigma}{\partial T}\right)_P \tag{11}$$

Dielectric saturation has already accounted for orientational effects of the molecules of water surrounding the ion, and so one must take a σ in keeping with the arrangement of the molecules in the bulk of the liquid. Since the molecules in the bulk of the liquid have a different arrangement from those of the surface molecules, σ cannot be equated with the normal surface tension of water. The following procedure is used to calculate an approximate value for σ.

Stefan[37] postulated that the energy gained by a molecule on being transferred from the bulk of the liquid to its surface must be equal to the energy gained during a further transfer from the surface to the vapor. This means that E_s is equal to one-half the latent heat of vaporization. Difficulty arises in assigning a numerical value to $(\partial\sigma/\partial T)_P$ but we have adopted the approximation of Drakin and Mikhailov and used the temperature coefficient of the ordinary surface tension of water.

For water at 25° the change of surface tension with temperature is −0.155 erg cm^{-2} deg^{-1} and at 80°, −0.184 erg cm^{-2} deg^{-1}.[38] Using the standard latent heat of vaporization of water, E_s is obtained as 379.2 erg cm^{-2}; σ then becomes 333.0 and 314.2 erg cm^{-2} at the two temperatures. $\Delta G°_h$ is then $6.02 r_s^2$ kcal mole^{-1} at 25° and $5.68 r_s^2$ kcal mole^{-1} at 80°.

The function to express the free-energy change of solvation $\Delta G°_{sol}$ then becomes

$$\Delta G°_{sol} = \Delta G°_{el} + \Delta G°_h + \Delta G°_v \tag{12}$$

Calculations

Evaluation of the integral in eq 10 was carried out using a PDP-6 high-speed computer. Integrations were performed numerically using Simpson's rule in the program SOLVEN by W. A. Millen.

Standard free-energy changes of solvation at 25° are shown in Table I. Enthalpy changes were calculated from the temperature dependence of the free energies between 25 and 80°, and these are presented in Table II. Theoretical results were compared with experimental results using the conventions outlined by Rosseinsky.[39] Here, conventional thermodynamic quantities are given with respect to the gas-phase hydrogen ion. Thermodynamic solvation values, Y_{sol}, of any ion are related to those of hydrogen ion by

$$\Delta Y_{sol,con}(M^{Z+}) = \Delta Y_{sol}(M^{Z+}) - Z\Delta Y_{sol}(H^+) \tag{13}$$

The constancy of $\Delta Y_{sol}(H^+)$ values thus provides a means of gauging the accuracy of any calculation. Rosseinsky has recently reviewed the subject of hydra-

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Table II. Summary of Data for the Change in Standard Free Energy of Solvation of Ions in Water at 80° and the Change in Standard Enthalpy of Solvation[a]

Ion	Ionization, free energies[b]	$\bar{G}°(\mathrm{l})$	$\Delta G°_h$	$\Delta G°_v$	Σ(col 3–5)	$-\Delta G°_{sol}$	$-\Delta H°_{sol}$	$-\Delta H°_{sol}$ (H^+)
Na^+	119.18	11.27	7.78	2.36	21.41	97.8	104.9	268.7
K^+	100.76	5.91	12.61	2.36	20.88	79.9	83.1	267.1
Rb^+	97.00	4.67	15.11	2.36	22.14	74.9	76.2	266.2
Cs^+	90.47	3.35	19.65	2.36	25.36	65.1	63.8	261.6
Mg^{2+}	524.09	55.46	10.22	2.36	68.04	456.1	485.0	273.5
Ca^{2+}	415.81	30.62	16.02	2.36	49.00	366.8	384.1	262.5
Sr^{2+}	386.78	25.44	18.40	2.36	46.20	340.6	354.1	265.1
Ba^{2+}	352.46	17.74	24.08	2.36	44.18	308.3	316.0	263.1
Al^{3+}	1229.56	125.65	12.95	2.36	140.96	1088.6	1149.0	272.5
Sc^{3+}	1020.92	72.56	19.88	2.36	94.80	926.1	965.3	270.7
Y^{3+}	907.92	62.34	22.27	2.36	86.97	821.0	854.4	257.4
La^{3+}	864.33	43.73	29.02	2.36	75.11	789.2	811.7	269.7

[a] All thermodynamic quantities are given in kcal mole^{-1}. [b] At 353.16°K.

tion energies and concludes that the experimental value best representing the absolute protonic free energy of hydration is +260.5 kcal mole^{-1}, and we have adopted this standard in recording the experimental values of $\Delta G°_{sol}$ in Table I.

Agreement with experiment is pleasing for free energies of ions for all charge types. Percentage differences between theory and experiment are low and certainly within the range of expectation. The average $\Delta G°_{sol}(H^+)$ is -259.0 kcal mole^{-1} for all the ions, comparing well with the accepted experimental result. The relatively small difference in hydration free energies at 25 and 80° are well accounted for by the theory. With the exception of Cs^+ subsequent enthalpy changes show the correct trend in magnitude and in sign. A larger variation in $\Delta H°_{sol}(H^+)$ is found than for the free-energy change. However, this is to be expected since the method of determination depends on the difference between two large and similar terms.

Standard entropy changes of solvation are shown in Table III. These have been calculated from the difference in $\Delta G°_{sol}$ and $\Delta H°_{sol}$ at 25°. It is probably not surprising that $\Delta S°_{sol}(H^+)$ values for all ions show quite large variation. Once again this is, in part, due to the method of evaluation which depends on the differences between three large and similar terms. Nevertheless, the results do show the correct systematic trend.

Table III. Summary of Entropy Data for the Solvation of Ions in Water

Ion	$-\Delta S°_{sol}$	$-\Delta S°_{sol}$ (H^+)	$S°(g)$	$\bar{S}°(\mathrm{l})$ $\bar{S}°(H^+) = -1.1$	$\bar{S}°(H^+) = -1.1$[b]
Na^+	20.1	25.2	35.3	15.2	13.3
K^+	9.1	22.7	36.9	27.8	23.4
Rb^+	3.7	20.2	39.2	35.5	28.6
Cs^+	−3.7	...	40.6	43.3	30.7
Mg^{2+}	81.8	35.1	35.5	−46.3	−30.4
Ca^{2+}	49.0	25.4	37.0	−12.0	−15.4
Sr^{2+}	38.2	20.8	39.3	1.1	−11.6
Ba^{2+}	21.8	18.0	40.7	18.9	+1.8
Al^{3+}	171.0	46.1	35.8	−135.2	−78.2
Sc^{3+}	111.0	...	37.3	−73.7	...
Y^{3+}	94.6	...	39.4	−55.2	...
La^{3+}	63.7	...	40.7	−23.0	...

[a] Thermodynamic quantities are given in cal deg^{-1} mole^{-1}. [b] NBS Circular 500.

From the Sackur–Tetrode equation, the translational entropy, $S°(g)$, of the monatomic gaseous ions was calculated. Using the relation $\Delta S°_{sol} = \bar{S}°(\mathrm{l}) - S°(g)$ the standard partial molar entropy $\bar{S}°(\mathrm{l})$ for the ions was then evaluated. These are given in Table III. $\Delta S°_{sol}(H^+)$ quantities have been recorded for those ions for which $\Delta S°_{sol,con}$ quantities are accurately known. An average $\Delta S°_{sol}(H^+)$ of -27.1 cal deg^{-1} mole^{-1} gives the standard partial molar entropy of the hydrogen ion to be $\bar{S}°(H^+) = -1.1$ cal deg^{-1} mole^{-1}.

A number of values for $\bar{S}°(H^+)$ have been proposed. Rosseinsky quotes a range of -6 to -2 cal deg^{-1} mole^{-1}, in keeping with the work of many experimental and assigned values. It appears, however, that our result of -1.1 cal deg^{-1} mole^{-1} is the first to be calculated purely from estimated free energies and enthalpies. Because doubt exists as to the value of $\bar{S}°(H^+)$, tabulated data for $\bar{S}°(\mathrm{l})$ will vary. NBS Circular No. 500[40] takes $\bar{S}°(H^+) = 0$ by convention, while Laidler[22] and Breck and Lin[41] prefer $\bar{S}°(H^+) = -5.5$ cal deg^{-1} mole^{-1}. A list of $\bar{S}°(\mathrm{l})$ values for $\bar{S}°(H^+) = -1.1$ cal deg^{-1} mole^{-1} as well as for NBS Circular 500 quantities for $\bar{S}°(H^+) = -1.1$ cal deg^{-1} mole^{-1} are included in Table III.

Evaluation of Results

The consistency of the over-all results for $\Delta G°_{sol}(H^+)$ show that solvation free energies can be calculated without reference to experiment for the noble gas ions in water. Li^+ and Be^{2+} have not been treated since some doubt[28] exists regarding the ionic radius of Li^+.

The theory is successful in that the enthalpies and entropies are obtainable from the temperature dependence of the solvation free energy. The theory, by treating the solvent as continuous medium, obviates the necessity of a knowledge of the coordination number and the cation–water bond energy in enthalpy calculations.[42] This factor alone is of great importance if similar properties are to be estimated for ions in other solvents for which coordination numbers are not known.

Serious limitations of the theory exist in its mathematical construction. The dielectric saturation theory was originally derived for point changes and point dipoles

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(40) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

(41) W. G. Breck and J. Lin, *Trans. Faraday Soc.*, **61**, 2223 (1965).

(42) A. D. Buckingham, *Discussions Faraday Soc.*, **24**, 151 (1957).

and has been applied by us to the case of an ion with finite size and water molecules with real dipoles.

As in most existing theories, polarizabilities of the ions have not been considered. From a classical viewpoint, the orientated water dipoles can induce a dipole in the ion proportional to the polarizability of the ion. The total ionic field would then contain contributions from both the ion and the induced dipole fields. This contribution to the total ionic field would nevertheless be very small for most ions considered here.

It is hoped that the model adopted here for ions in the liquid phase will prove as successful in its application to other solvent systems as more experimental solvation energies become available, particularly as the solvent structure is likely to be less complex than that of water.

Charge-Transfer Interaction in Tetracyanoethylene Complexes of Pyrene and Naphthalene

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Abstract: Theoretical treatments were made on the charge-transfer interaction between donor and acceptor in the tetracyanoethylene (TCNE) complex of naphthalene and that of pyrene with the consideration of the effect of interaction of higher energy charge-transfer configurations, and structural models were proposed for these complexes. The spectrophotometric investigation was carried out on the formation of the pyrene–TCNE complex in carbon tetrachloride. The dipole moment of the pyrene–TCNE complex was experimentally determined as 2.0 D. These experimental results and the corresponding data on the naphthalene–TCNE complex are compared with the results of theoretical treatment. It is shown that theoretical predictions consistent with the observations are obtainable when the higher energy charge-transfer configurations are taken into account.

The interaction between electron donor and acceptor in a molecular complex can be well understood by the charge-transfer theory developed by Mulliken.[1] According to the theory, the electronic structure of a 1:1 complex can be described as the resonance hybrid between the "no-bond structure" and the "dative structure." The ground-state wave function of a complex is generally expressed as

$$\Psi_N(\mathrm{D\cdot A}) = a\Phi_0(\mathrm{D\cdot A}) + b\Phi_1(\mathrm{D^+\cdot A^-})$$

where $\Phi_0(\mathrm{D\cdot A})$ and $\Phi_1(\mathrm{D^+\cdot A^-})$ are respectively the wave function of the no-bond structure and that of the dative structure. A simplifying assumption has been usually adopted on the wave function of the dative structure; namely, it can be approximately described with the wave function of the lowest energy charge-transfer configuration, *i.e.*, the state where an electron has been transferred from the highest occupied molecular orbital of the donor to the lowest vacant molecular orbital of the acceptor. A number of investigations on the molecular complexes have been carried out on the basis of this assumption. This simplifying assumption is quite useful; however, its general validity is obviously questionable. The significance of higher energy charge-transfer configurations, including back charge-transfer configurations, has been pointed out by Mulliken[2] and several other investigators.[3–5]

In a previous paper[4] we have shown that the mixing of higher energy charge-transfer configurations is of great importance in the case of the pyrene–tetracyanoethylene complex, particularly in the appearance of its multiple charge-transfer bands. Seemingly this is the case not only in this particular complex, but also in many other π complexes which involve polycyclic aromatics as the electron donor. Thus it is of particular interest to elucidate various aspects associated with the effect of the mixing of higher energy charge-transfer configurations by making a detailed study on some typical examples of these complexes. The complexes which involve naphthalene or pyrene as the donor and tetracyanoethylene (TCNE) as the acceptor seem to be most suited for this purpose, since, firstly, the component molecules possess a rather simple molecular structure with high symmetry, and, secondly, we can expect that the charge-transfer interaction between the donor and acceptor plays an important role in the intermolecular binding in these complexes because TCNE is a nonpolar molecule with a very high electron affinity.

Spectrophotometric investigations on the complex formation in carbon tetrachloride have been already carried out in detail on the naphthalene–TCNE complex.[6,7] The dipole moment of this complex also has been determined. Compared with this, available experimental data are limited on the pyrene–TCNE complex. Therefore, in the present study, we have carried out the spectrophotometric investigation on the

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