SOLVATION NUMBERS OF IONS

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Contents

I. Introduction

From soon after the inception of theory of electrolytes until the present, the chemical literature is replete with articles dealing with the measurement, magnitude, and influence on chemical phenomena in solution of the solvation numbers of ions. No recent or extensive summary of such data has been compiled. The purpose of this review is to assemble and compare data on solvation numbers reported up to 1969.

II. Methods of Measurement

A. TRANSFERENCE

1. Theoretical and Experimental

The transference or transport number of an ion is the fraction of the total current carried by that ion. Since the velocities of the two ions of an electrolyte are not equal, different concentration changes will occur in the regions of the cathode and anode, respectively, and these changes may be used to evaluate transference numbers.[1,2]

In general, for an ith-type ion, the transport number is given by the expression

$$t_i = n_i u_i e_i / \sum n_i u_i e_i \qquad (1)$$

where n_i is the number of the ith-type ions per cubic centimeter, and u_i and e_i are the velocity and charge, respectively, of this type of ion. Since $e_i = z_i \epsilon_i$, where z_i is the valence and ϵ_i the electronic charge, then

$$t_i = n_i u_i z_i / \sum n_i u_i z_i \qquad (2)$$

where the summation in the denominators of eq 1 and 2 are taken over all the ions in solution.

Hittorf's method consists of chemically analyzing the contents of various portions of the solution of an electrolytic cell, and of ascertaining the faradays which flow through the cell using a silver or other type coulometer, or other current measuring device in series with the cell.

Washburn[3] has given a formula for the calculation of the transference number, t, of an ion formulated as follows. Let N_0 and N_F be the number of equivalents of an ion associated initially and finally with a given weight of solvent. Let N_E be the number of equivalents of this ion added to the solvent by the electrode reaction, and tN_E be the number of equivalents of this ion lost to the solvent by migration. Then

$$N_E - N_0 = N_E - N_E t \qquad (3)$$

wherefore

$$t = \frac{N_0 - N_E + N_E}{N_E} \qquad (4)$$

The moving boundary method of transference numbers is based on the fact that when a solution of one electrolyte is placed above a solution of another electrolyte in a tube and a direct current is passed from bottom to top, the boundary between the two solutions will become sharp and will move up the tube.

Let V be the volume in liters swept out per faraday of current passed, and VC be the equivalents of selected ion constituent passing per faraday a fixed plane in the tube, where C is the equivalents per liter of the selected ion. Also let I be the constant current flowing for τ seconds.

$$t = VCF/\tau I \qquad (5)$$

The moving boundary method can be used under certain conditions to measure the transference number of ion constituents in mixtures of electrolytes.

MacInnes[4] discusses in detail methods of forming the boundary and of making the measurements.

2. Solvation of Ions: "True" Transference Numbers

Transference number measurements may be used to determine the solvation of ions in solution. In the case of water solvent, solvation is termed hydration.

"True" transference numbers are those obtained by a method which is not influenced by the movement of solvents of solvation. Among the early workers in the field of solvation

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[1] W. Hittorf, *Z. Physik. Chem.*, **39**, 612 (1901).

[2] W. Hittorf, *ibid.*, **43**, 239 (1903).

[3] E. W. Washburn, "Principles of Physical Chemistry," McGraw-Hill, New York, N. Y., 1921, p 276.

[4] D. A. MacInnes, "The Principles of Electrochemistry," Reinhold, New York, N. Y., 1939, Chapter 4.

using the Hittorf method were Nernst,[5] Buchböck,[6] Washburn,[7,8] and their associates. A second solute, *e.g.*, sucrose or raffinose, was included in the solution in the Hittorf cell. The changes in salt and solvent concentrations were referred to the second solute. The second substance, being composed of neutral molecules, was uninfluenced by the passage of the electric current. However, the ratio of the reference substance to the water was changed in the electrode regions of the cell if the solvent was carried along by the moving ions. By determining accurately the concentration of the reference substance, the "true" transference number of the ion constituent and Δn, the increase or decrease of the number of moles of water, in a given electrode portion per faraday of electricity passed was calculated. A polarimeter was used by Washburn[9-16] to determine the concentration of reference substance.

Taking Δn as the net effect of the solvent carrying by all the ions present, for the cathode portion in the case of a binary electrolyte Δn becomes

$$\Delta n = \tau_c n_s^{c} - \tau_a n_s^{a} \tag{6}$$

where τ_c and τ_a are the "true" transference numbers of the cation and anion, respectively, and n_s^c and n_s^a are the number of moles of solvent carried per mole by cation and anion. These differences in terms of the moles of solvent carried per mole of cation as a function of the moles of solvent carried per mole of anion can be written from eq 6 as follows.

$$n_s^{c} = \frac{\Delta n}{\tau_c} + \frac{\tau_a}{\tau_c} n_s^{a} \tag{7}$$

Mixed solvents are now used extensively, and since true transference numbers are used in electrochemical calculations, methods of obtaining these and the solvation numbers of ions in mixed solvents have been devised[17] using Washburn's equation for the difference between the true transference number, τ, and the Hittorf transference number, t. Equation 8 was obtained where $\Delta g^{F}{}_{sol}$ is the grams of solvent transferred per faraday, g_{sol} the grams of solvent, and n_s the equivalents of solute in n_{sol} moles of solvent.

$$\tau - t = \Delta g^{F}{}_{sol} \frac{n_s}{g_{sol}} \tag{8}$$

From the above equation true transference numbers can be found from Hittorf ones without having a knowledge of the molecular weight of the solvent.

With true transference relations 9 and 10 can be written for a solvent containing two components A and B. In these

$$\Delta g^{F}{}_{(sol)A} = M_{(sol)A} n^{c}{}_{(sol)A} \tau^{c} - M_{sol(A)} n^{a}{}_{(sol)A} \tau^{a} \tag{9}$$

$$\Delta g^{F}{}_{sol} = [M_{(sol)A} n^{c}{}_{(sol)A} + M_{(sol)B} n^{c}{}_{(sol)B}]\tau^{c} - [M_{(sol)A} n^{a}{}_{(sol)A} + M_{(sol)B} n^{a}{}_{(sol)B}]\tau^{a} \tag{10}$$

equations $\Delta g^{F}{}_{(sol)A}$ and $\Delta g^{F}{}_{sol}$ are respectively grams of solvent A and total grams of solvent, transferred from the anode to the cathode; $M_{(sol)A}$ and $M_{(sol)B}$ are respectively the molecular weights of solvent components A and B; $n^{c}{}_{(sol)A}$ and $n^{c}{}_{(sol)B}$ are respectively the moles of solvent component A and B solvating the cation; $n^{a}{}_{(sol)A}$ and $n^{a}{}_{(sol)B}$ are respectively the moles of solvent components A and B solvating the anion; and τ^{c} and τ^{a} are respectively the true transference numbers of the cation and anion.

Dividing eq 9 by $M_{(sol)A}$ gives for a pure solvent eq 6. Equation 6 has an infinite number of solutions, but these can be reduced by assuming that $n_{(sol)A}$ and $n_{(sol)B}$ must be integers and have upper and lower limits.

A reasonable lower limit would be zero for the values of $n_{(sol)A}$ and $n_{(sol)B}$ for an unknown system. The maximum upper limit for $n^{c}{}_{(sol)A}$ would be the moles of solvent A per mole of cation in the solution assuming the anion is not solvated, and the maximum upper limit of $n^{a}{}_{(sol)A}$ would be the moles of solvent per mole of anion in the solution assuming the cation is not solvated, and similarly for $n^{c}{}_{(sol)B}$ and $n^{a}{}_{(sol)B}$. The total number of moles of solvent A solvating the ions must not exceed the moles of solvent A in the solution. The relation

$$n^{c}{}_{(sol)A} + n^{a}{}_{(sol)A} \leqq \frac{n_{(sol)A}}{n_s} \tag{11}$$

can be stated where $n_{(sol)A}$ is the total moles of solvent A in the solution and n_s is the equivalents of solute. Equation 11 can be programmed and solved for all possible values of the integers, provided the necessary transference and solution data are available. Equation 10 can be expanded and eq 9 substituted into it to give

$$\frac{\Delta g^{F}{}_{sol} - \Delta g^{F}{}_{(sol)A}}{M_{(sol)B}} = n^{c}{}_{(sol)B}\tau^{c} - n^{c}{}_{(sol)B}\tau^{a} \tag{12}$$

Equation 12 can be solved in the same manner as eq 11.

Remy and coworkers[18] determined differences in ionic hydration by measuring the volume change in the two halves of a solution separated from each other by a parchment paper membrane in a cell through which current was passed. Change in volume due to electroosmosis of the solvent alone was negligibly small in 1.0 *N* electrolyte solutions at which concentrations their measurement were made (see also the work of Baborousky).[19]

3. Solvation Numbers

MacInnes[4] calculated, employing eq 7, the number of moles of water carried per mole of cation for different assumed hydrations of the chloride ion (see Table I).

In the studies of Remy[18] parchment paper served as the reference boundary with respect to which volume changes in the electrode regions were measured. MacInnes[4] shows that in the case of the indifferent reference substance

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(5) W. Nernst, C. C. Gerrard, and E. Oppermann, *Nachr. Kgl. Ges. Wiss. Gottengin*, **56**, 86 (1900).

(6) G. Buchböck, *Z. Physik. Chem.*, **55**, 563 (1906).

(7) E. W. Washburn, *J. Amer. Chem. Soc.*, **31**, 322 (1909); *Z. Physik. Chem.*, **66**, 513 (1909).

(8) E. W. Washburn and E. B. Millard, *J. Amer. Chem. Soc.*, **37**, 694 (1915).

(9) D. M. Mathews, J. O. Wear, and E. S. Amis, *J. Inorg. Nucl. Chem.*, **13**, 298 (1960).

(10) W. Ves Childs and E. S. Amis, *ibid.*, **16**, 114 (1960).

(11) J. O. Wear, C. V. McNully, and E. S. Amis, *ibid.*, **18**, 48 (1961).

(12) J. O. Wear, C. V. McNully, and E. S. Amis, *ibid.*, **19**, 278 (1961); **20**, 106 (1961).

(13) J. O. Wear, J. T. Curtis, Jr., and E. S. Amis, *ibid.*, **24**, 93 (1962).

(14) J. A. Bard, J. O. Wear, R. G. Griffin, and E. S. Amis, *J. Electroanal. Chem.*, **8**, 419 (1964).

(15) R. G. Griffin, E. S. Amis, and J. O. Wear, *J. Inorg. Nucl. Chem.*, **28**, 543 (1966).

(16) J. R. Bard, E. S. Amis, and J. O. Wear, *J. Electroanal. Chem.*, **11**, 296 (1966).

(17) J. O. Wear and E. S. Amis, *J. Inorg. Nucl. Chem.*, **24**, 903 (1962).

(18) H. Remy, *Z. Physik. Chem.*, **118**, 161 (1925); **124**, 41, 394 (1926).

(19) G. Baborousky, *ibid.*, **129**, 129 (1927).

method the number of moles of water transferred per faraday, Δn of eq 7, in various electrolytes in 1.0 N solutions were identical with the number of moles of water carried per faraday in 1.3 N solutions except for hydrochloric acid which shows a small variation in the two concentrations (see Tables X and XI of Chapter 4 of ref 4). He also compares Δn values for the indifferent reference substance and the parchment paper methods (see Table IX, Chapter 4). Since the Δn values at the two concentrations of electrolytes are almost identical using the indifferent reference substance approach, probably "true" and Hittorf transference numbers each have the same values for the same electrolyte at the two concentrations. The values of n_s^c were calculated from eq 7 for the cations of HCl, KCl, NaCl, and LiCl for the parchment paper data using $n_s^a = 4$ for the chloride ion (Table I). The n_s^c for the various cations in the case of the indifferent reference substance and in the case of parchment paper approach each other.

Washburn[7] reported Hittorf transference measurement of H^+, Li^+, Na^+, Rb^+, and Cs^+ ions at 25° in 1.25 N solution for $n_s^{Cl^-}$ equal to 4 and 9. The data for $n_s^{Cl^-}$ equal to 9 quoted by Glasstone[20,21] are given in Table I.

From Hittorf data[12,13] at 25° using an inert reference, Wear and Amis,[17] employing eq 9, calculated the maximum and minimum values for the moles of water and of ethanol in multiples of four solvating the cations and anions of LiCl in various weight per cents of the ethanol component of the solvent. Similar calculations were made using eq 9 for the cations and anions of KCl in water. The maximum and minimum number of moles of water and of ethanol transported at 25° by Li^+ and Cl^- ions at different weight per cents of ethanol in water solvents, and for K^+ and Cl^- ions in water, are recorded in Table I. For lithium chloride the trends indicated in the table are what is expected, except for the maximum number of moles of water around the anion. The authors felt that either the value at 80 wt % ethanol is too low or the value at 90 wt % ethanol is too high, since the primary solvation shell of lithium ion is four molecules in both water[20] and ethanol[22] and the primary solvation shell of chloride ion[23] is eight molecules of water. Wear and Amis[17] assumed that solvation occurs in multiples of four. In addition hydrogen ion combines with four waters to form the pyramidal $H_9O_4^+$ complex stable up to 100°[24] and it was found that much hydration is a buildup of tetrahedrons.[25] The most common buildup appears to be a dodecahedron, which is five tetrahedrons. This is probably sound reasoning since the structure of water is tetrahedral and secondary solvation is probably greatly influenced by water structure as well as statistics, electrostatics, and chemical affinity.

A discrepancy between the numerical transport of water and the transport values of the cations found from cathodic or anodic determinations in the case of chlorides, bromides, and iodides of the alkali metals, the alkaline earth metals, and hydrogen was traced to the swelling of the parchment membranes caused by the electrolytes with a consequent decrease in mobility of the anions.[26]

A distinction has been made[27-29] between close or chemical hydration and the wider or physical hydration complex ions, presumably in chemical hydration complex ions form. Physical hydration, considered a hydrodynamic phenomenon, is due to electrostatic attraction of the solvent dipoles by an ion. It was felt that no method existed for the determination of chemical hydration alone.

A comparison of the solvation numbers in normal solutions of several salts determined by the parchment paper, salting-out, and diffusion methods has been made.[27] Assuming the chloride ion to have a solvation number of 4, the solvation numbers of the other ions have the following ranges: Na^+, 8–17; K^+, 5–14; Li^+, 13–15.5; Br^-, −3–7.5, and I^-, 2–5. A comparison of the solvation of certain ions in 1 and 0.1 N solutions, respectively, show[29] the values: Li^+, 13–14–62; K^+, 5–29.3; Cl^-, 4–26.6; I^-, 2–31.4.

Solvation numbers of other ions have been measured using the parchment paper method;[30,31] see Table I.

The solvation numbers listed in Table I (ref 28) for K^+, Na^+, Li^+, Cl^-, and Br^- ions were checked,[32] and the transport number of the hydrogen ion was determined. This paper lists the hydration numbers of the above ions as determined[33] using their activities.

The solvation of the ions of LiCl was studied[34] using camphor as the inert substance in Hittorf experiments in methyl, ethyl, and *n*-propyl alcohol solvents. In a given alcohol the solvation of the lithium ion decreased with increasing concentration of the LiCl.

It was observed[35] through ion hydration derived from the transport of water that Kohlrausch's law of independent migration of ions is not exact in fairly concentrated solutions. Also, for concentrated solutions the electroosmotic transport does not interfere with electrolytic transport in the determination of hydration.

The hydration of the SO_4^{2-} ion was determined[36] using three parchment paper diaphragms in a four-compartment cell; see Table I.

It was concluded[37] that all methods used to date on ion hydration were open to objections, but the most promising method involved ultrasonic vibrations.

The agreement in transference number values with neutral solutions obtained by the analysis of the anode and cathode layers suggests[38] that the high hydration values ascribed[39,40] to alkali metal cations in dilute solution by transference measurements, with or without a reference substance, are spurious.

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(38) L. Nickels and A. J. Allmand, *J. Phys. Chem.*, **41**, 873 (1937).

(39) H. Remy, *Z. Physik. Chem.*, **118**, 161 (1926).

(40) J. Velisek, *Chem. Listy*, **20**, 242 (1926).

Table I

Solvation of Various Ions by Different Electrolytic Transference Methods

Solvent	*Ref ion*	*Assumed solvation no. n of ref ion*	*Solvated ion*	*Solvation no. n of ion*	*Concn of electrolyte, N*[c]	*Temp, °C*	*Ref no.*
Water	Cl^-	0	H^+	0.3	1.2	25	4[a]
Water	Cl^-	4	H^+	1.0	1.2	25	4[a]
Water	Cl^-	8	H^+	1.8	1.2	25	4[a]
Water	Cl^-	0	Cs^+	0.7	1.2	25	4[a]
Water	Cl^-	4	Cs^+	4.7	1.2	25	4[a]
Water	Cl^-	8	Cs^+	8.9	1.2	25	4[a]
Water	Cl^-	0	K^+	1.3	1.2	25	4[a]
Water	Cl^-	4	K^+	5.4	1.2	25	4[a]
Water	Cl^-	8	K^+	9.5	1.2	25	4[a]
Water	Cl^-	0	Na^+	2.0	1.2	25	4[a]
Water	Cl^-	4	Na^+	8.4	1.2	25	4[a]
Water	Cl^-	8	Na^+	14.9	1.2	25	4[a]
Water	Cl^-	0	Li^+	4.7	1.2	25	4[a]
Water	Cl^-	4	Li^+	14.0	1.2	25	4[a]
Water	Cl^-	8	Li^+	23.0	1.2	25	4[a]
Water	Cl^-	4	H^+	1.2	1.0	25	4[b]
Water	Cl^-	4	K^+	5.0	1.0	25	4[b]
Water	Cl^-	4	Na^+	9.8	1.0	25	4[b]
Water	Cl^-	4	Li^+	14.3	1.0	25	4[b]
Water	Cl^-	4	H^+	1.0	1.2	25	8
Water	Cl^-	4	Cs^+	4.7	1.2	25	8
Water	Cl^-	4	K^+	5.4	1.2	25	8
Water	Cl^-	4	Na^+	8.4	1.2	25	8
Water	Cl^-	4	Li^+	14.0	1.2	25	8
58% EtOH	Cl^-	18 (max H_2O)	Li^+	50 (max H_2O)	0.361 *M*	25	17
58% EtOH	Cl^-	0 (min H_2O)	Li^+	11 (min H_2O)	0.361 *M*	25	17
58% EtOH	Cl^-	13 (max EtOH)	Li^+	22 (max EtOH)	0.361 *M*	25	17
58% EtOH	Cl^-	2 (min EtOH)	Li^+	0 (min EtOH)	0.361 *M*	25	17
80% EtOH	Cl^-	4 (max H_2O)	Li^+	28 (max H_2O)	0.386 *M*	25	17
80% EtOH	Cl^-	0 (min H_2O)	Li^+	15 (min H_2O)	0.386 *M*	25	17
80% EtOH	Cl^-	17 (max EtOH)	Li^+	29 (max EtOH)	0.386 *M*	25	17
80% EtOH	Cl^-	3 (min EtOH)	Li^+	0 (min EtOH)	0.386 *M*	25	17
90% EtOH	Cl^-	10 (max H_2O)	Li^+	8 (max H_2O)	0.333 *M*	25	17
90% EtOH	Cl^-	5 (min H_2O)	Li^+	0 (min H_2O)	0.333 *M*	25	17
90% EtOH	Cl^-	17 (max EtOH)	Li^+	43 (max EtOH)	0.333 *M*	25	17
90% EtOH	Cl^-	0 (min EtOH)	Li^+	7 (min EtOH)	0.333 *M*	25	17
H_2O	Cl^-	69 (max H_2O)	K^+	74 (max H_2O)	0.373 *M*	25	17
H_2O	Cl^-	0 (min H_2O)	K^+	3 (min H_2O)	0.373 *M*	25	17
H_2O	Cl^-	52 (max H_2O)	K^+	62 (max H_2O)	0.505 *M*	25	17
H_2O	Cl^-	0 (min H_2O)	K^+	2 (min H_2O)	0.505 *M*	25	17
H_2O	Cl^-	4	Na^+	8–9	1		28
H_2O	Cl^-	4	K^+	5	1		28
H_2O	Cl^-	4	Li^+	13–14	1		28
H_2O	Cl^-	4	Br^-	3–4	1		28
H_2O	Cl^-	4	I^-	2	1		28
H_2O	Cl^-	4	H^+	1	1		30
H_2O	Cl^-	4	Mg^{2+}	20	1		31
H_2O	Cl^-	4	Ca^{2+}	17–16	1		31
H_2O	Cl^-	4	Sr^{2+}	16	1		31
H_2O	Cl^-	4	Ba^{2+}	11	1		31
H_2O	Cl^-	4	H^+	1.06	1		32
H_2O	Cl^-	4	SO_4^{2-}	2.8	1		36
H_2O	Cl^-	4	SO_4^{2-}	1.4	1		41
H_2O	Cl^-	4	K^+	5	1		41
H_2O	Cl^-	3.0	Na^+	7.4	1		42
H_2O	SO_4^{2-}	10.7	Cu^{2+}	10.7	1		42
H_2O	Cu^{2+}	8.5	$CuCl_4^-$	19.7	1		42
H_2O	Na^+	5	SO_4^{2-}	1.35	1		47
H_2O	K^+	5	NO_3^-	4.58	1		47
H_2O	Na^+	5	NO_3^-	4.54	1		47
H_2O	Li^+	7	H^+	0.5			57
H_2O	Li^+	7	Na^+	5			57
H_2O	Li^+	7	K^+	2			57

Table I (Continued)

Solvent	*Ref ion*	*Assumed solvation no. n of ref ion*	*Solvated ion*	*Solvation no. n of ion*	*Concn of electrolyte, N*[c]	*Temp, °C*	*Ref no.*
H_2O	Li^+	7	Cs^+	1.5			57
H_2O	Li^+	7	Ba^{2+}	9.5			57
H_2O	Li^+	7	Cd^{2+}	11			57
H_2O	Li^+	7	Cl^-	1			57
H_2O	Cl^-	5	Li^+	22	0.3		59
H_2O	Cl^-	5	Na^+	13	0.3		59
H_2O	Cl^-	5	K^+	7	0.3		59
H_2O	Cl^-	5	Cs^+	6	0.3		59
H_2O	Cl^-	5	Mg^{2+}	36	0.3		59
H_2O	Cl^-	5	Ca^{2+}	29	0.3		59
H_2O	Cl^-	5	Sr^{2+}	29	0.3		59
H_2O	Cl^-	5	Ba^{2+}	28	0.3		59
H_2O	Cl^-	5	Cu^{2+}	34	0.3		59
H_2O	Cl^-	5	Zn^{2+}	44	0.3		59
H_2O	Cl^-	5	Cd^{2+}	39	0.3		59
H_2O	Na^+	13	Br^-	5	0.3		59
H_2O	Cl^-	5	F^-	7	0.3		59
H_2O	Cl^-	5	NO_3^-	6	0.3		59
H_2O	Na^+	13	CH_3COO^-	11	0.3		59
H_2O	Cl^-	5	SO_4^{2-}	12	0.3		59
NMA	R_4N^+	0	Li^+	5.1		40	66
NMA	R_4N^+	0	Na^+	3.5		40	66
NMA	R_4N^+	0	K^+	3.3		40	66
NMA	R_4N^+	0	Cs^+	2.6		40	66
NMA	R_4N^+	0	NH_4^+	2.7		40	66
NMA	R_4N^+	0	Cl^-	2.1		40	66
NMA	R_4N^+	0	Br^-	1.7		40	66
NMA	R_4N^+	0	I^-	1.5		40	66
NMA	R_4N^+	0	CN^-	1.3		40	66
NMA	R_4N^+	0	NO_3^-	1.5		40	66
NMA	R_4N^+	0	Ba^{2+}	9.0		40	66
NMA	R_4N^+	0	Sr^{2+}	8.6		40	66
NMA	R_4N^+	0	Ca^{2+}	8.6		40	66
NMA	R_4N^+	0	Mg^{2+}	10.3		40	66

[a] Inert reference substance. [b] Parchment paper. [c] Except where noted.

The hydration of sulfate ions was measured[41] using semipermeable membranes in electrolytic transport experiments; see Table I.

Ionic water transport was found[42] to be independent of the specific effects of the paper diaphragm used at concentrations of 0.8 *N* and greater. In more dilute solutions the electroendosmotic effect is important. Solvation numbers are listed in Table I.

The electroosmotic and electrolytic transports of water through parchment membrane in contact with $CuCl_2$ and $CuSO_4$ were determined.[43] The electroosmotic transport was much greater for $CuSO_4$. Valency alone could not account for the great effect of the sulfate ion. Electrolytic transport of water per faraday[44] presumably does not increase with decreasing concentration of $CuSO_4$ from 0.4 *N*. From 0.0005 to 0.2 *N* there is a composite effect of a constant electrolytic water transport and of an electroendosmotic action by the parchment diaphragm. A diaphragm of powdered glass has been used[45] for measuring liquid transport for a constant applied potential using solutions of $CuSO_4$. For solutions greater than 0.005 *N*, the liquid transport per faraday is related to the dilution by a linear law and decreased to a negligible value at 0.1 *N* solution.

The transport of water to electrodes through benzaldehyde or carbon tetrachloride has been measured.[46] Hydration of ions were investigated[47] using a three-parchment membrane setup. Data are listed in Table I.

MacDonald[48] using the mobility of hydrogen ion as about 65 estimated the hydrated ion to be H_3O^+. He points out that Darmois' method[49] would lead to negative values of hydration for chloride and potassium ions, and 0.3, 1, and 5, respectively, for the hydration numbers of H^+, Na^+, and Li^+ ions.

The apparent hydration numbers of migrating ions have been calculated[50] using mobility.

The concept of a fixed hydration number and of a definite Stokes radius of an ion has been discussed.[51] The total hydra-

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tion energy of an ion is due first to the nearest surrounding molecules, which may either increase or decrease the energy of the system ion–water; and, secondly, to the sum of the actions of the more remote water molecules, which always decreases that energy. The activation energy of viscosity and the mean time of stay of the water molecules nearest to the ion is increased by hydrated ions, but decreased by nonhydrated ions giving negative hydration. Darmois' interpretation[52,53] of observations that the temperature coefficient of the mobility of hydrated ions is greater than that of the viscosity of water, due to progressive dehydration with increasing temperature and the corresponding decrease in Stokes radii of the ions, was criticized because it failed to recognize the difference existing between the temperature coefficients of the mobilities of the hydrated and unhydrated ions and the temperature coefficient of the viscosity of the solvent.

It was assumed[54–57] that a hydration flux exists and thus a hydrodynamic reflux, whose effect modifies the transport number of ions. Ionic mobilities are taken as the sum of the mobilities of the ions in an immobile medium and the speed of entrainment due to hydrodynamic reflux. This view on the intervention of ion hydration helps explain the inversion of the Hittorf phenomenon.

Haase[58] using electrolytic water transport measurements obtained the data listed in Table I.

Three cellophane membranes were used[59] in a four-compartment vessel filled with 0.3 *N* electrolyte solution. The solvent was D_2O in compartments 1 and 2 and H_2O in 3 and 4; see Table I for data.

The effect of the hydration of ions on orientation in solutions of electrolytes was formulated[60] in terms of a modified Kohlrausch rule. It was found[61] in the range of 2–11 *N* LiCl at 20° that the average number of molecules of water carried by Li^+ ion displaced by an electric field decreased with increasing concentration. This was termed the kinetic hydration number of Li^+ ions.

Selective solvation of ions in solvent mixtures has been studied[62–64] using a transference technique. The data are in Table II. For $CaCl_2$ in water–methanol mixtures, the change in the composition of the solvent due to hydrolysis was determined from the densities and refractive indices of the solutions. The solvation number of Li^+ ion in Li_2SO_4 was found to decrease[65] from 9 in 2 *N* to 5 in 5.5 *N* aqueous solutions.

Appreciable ion–solvent interaction was observed[66] in KBr solutions in *N*-methylacetamide (NMA). The solvation numbers of various ions in NMA are in Table I. The improved method of Robinson and Stokes[67] as proposed by Nightingale[68] was used in the calculations in which the tetraalkylammonium ions R_4N^+ except $(CH_3)_4N^+$ were assumed to be unsolvated.

Table II

Solvent	*Salt*	*Ion selectively solvated*	*Solvent component selectively solvating the ion*	*Ref*
H_2O-CH_3CN	$AgNO_3$	Ag^+	CH_3CN	61
H_2O-CH_3CN	$AgNO_3$	NO_3^-	H_2O	61
H_2O-CH_3OH	$CaCl_2$	Ca^{2+}	H_2O	62
H_2O-CH_3OH	$CaCl_2$	Cl^-	H_2O	62
H_2O-hydrazine	$ZnCl_2$	Zn^{2+}	Hydrazine	63
H_2O-hydrazine	$ZnCl_2$	Cl^-	H_2O	63
H_2O-acetonitrile	$ZnCl_2$	Zn^{2+}	H_2O	63
H_2O-acetonitrile	$ZnCl_2$	Cl^-	H_2O	63

Solvation of the ions of hydrochloric and of *p*-toluenesulfonic acids in formic acid solutions were studied[69] by electrolysis of 0.8–0.2 *N* hydrochloric acid and 1.0–0.2 *N p*-toluenesulfonic acid solutions using $H^{14}CO_2H$ as a tracer. The mobilities of anion and cation were assumed equal. More $H^{14}CO_2H$ was transported into the cathode than into the anode space. The solvation numbers of the Cl^- and $MeC_6H_4SO_3^-$ were approximately the same and independent of the concentration. The solvation number of the cation tended to increase with decreasing concentration of the electrolyte.

In a moving boundary electrical transport investigation of magnesium sulfate, magnesium chloride, and magnesium nitrate solutions, it was found[70] that the unsymmetric nature of the electrolyte affected the hydration of the ions. For magnesium sulfate solutions there was a substantial transfer of solvent toward the cathode: 12 and 8.7 mol of water per F, respectively, at 3 and 5 *N*. In the cases of $MgCl_2$ and $Mg(NO_3)_2$ there was an insignificant transfer of solvent toward the anode.

Moving boundary hydration numbers, *n*, of H^+, Li^+, Na^+, and K^+ ions in highly concentrated solutions of chlorides were determined[71] using indicator electrolytes at 20° and, with the exception of H^+, arranged in reversible dependence on their radii. Thus $n_{Li^+} > n_{Na^+} > n_{K^+}$. At low concentrations of HCl, the H^+ ions have a maximum mobility, mainly of a "relay" character, and a minimum hydration. In higher concentrations of HCl the H^+ ions are hydrated H_3O^+ ions. The "relay" and the negative mobilities of the H^+ ion decreased as the HCl increased in concentration. At maximum HCl concentrations H_3O^+ determines the ion's mobility.

Water transport in cation-exchange membranes was reported[72–74] to depend on current density in 0.01 *N* electrolyte solution. Two cation-exchange membranes, cross-linked

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phenolsulfonic acid (PSA) and polyethylene–styrene graft copolymer (AMF), were used. The moles, l_w, of water transported per faraday passed in high water content membranes were high at low current densities and low at high current densities for the alkali metal ions and similarly for the low water content membranes for Li^+, Na^+, and K^+ ions, whereas l_w for Rb^+ and Ca^+ ions was significantly affected by current density. Table III contains the data.[72]

Table III

Number of Moles of Water, l_w, Transported across Cation-Exchange Membranes in Contact with 0.01 *N* Solutions of Alkali Metal Chlorides as a Function of Current Density at 25°

Current density, mA/cm²	l_w				
	Li⁺	*Na⁺*	*K⁺*	*Rb⁺*	*Cs⁺*
		PSA Membrane			
0.32	72.6	62.1	55.5	45.5	46.9
1.58	42.6	39.3	34.2	33.4	30.8
3.15	36.9	32.9	27.7	26.2	25.8
15.75	27.6	24.7	20.3	19.5	19.6
		AMF Membrane			
0.32	12.1	9.6	7.1	4.9	4.8
1.58	10.3	7.0	4.7	4.9	4.9
3.15	10.3	7.0	4.5	4.5	4.9
15.75	10.1	6.9	4.2	4.6	5.0

The PSA membrane data confirm[75–91] the current density dependence of l_w in 0.01 *N* solutions. The data from comparatively low content AMF membranes support both the dependence and independence of l_w on current density. The two factors determining the dependence of l_w on current density are membrane water content (or pore size) and the size of the ion. Conditions existing at the membrane–solution interface and within the membrane affect the variation of l_w with current density. Concentration polarization, which contributes to the interfacial phenomena involved, was eliminated by efficient stirring of solutions and using low currents.

Dependence of electroosmotic water transport on current density across a polystyrenesulfonic acid cation-exchange membrane in contact with sodium chloride solutions (0.1, 1.0, and 4.0 *M*) was reported.[83]

Generally, unstirred solutions were used[84–87] to measure water transport across cation-exchange membranes. Data by this method have been verified by independent measurements of membrane potentials.[88] Conceivably, some concentration polarization might occur in very dilute solutions. No significant liquid film resistance in concentrated solutions[89] was observed. Stirring did not eliminate the current dependence of electroosmotic water transport. The major influences on this phenomenon for a given cation appear to be (1) the internal concentration of the membrane pore solution and (2) the current density.[73]

The lack of effect of stirring on electroosmosis is confined to current density ranges in which counterion transport number remained unaffected and l_w is unity. This is a membrane transport phenomenon which is not well understood and occurs with an almost asymptotic rise of l_w with decrease in current density. This Bethe–Toropoff[90,91] effect, due to concentration polarization at the solution–membrane interface, mainly leads to membrane polarization and can be eliminated by stirring the solutions on either side of the membrane.

In Table I there is variation among the solvation numbers of a given ion, but there are certain consistent trends. The order of the solvation numbers of the alkali metal ions is $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. The more dilute the solution the greater the solvation of a given ion. The alkaline earth metal ions are more highly solvated than the alkali metal ions. The order of the solvation of the alkaline earth ions tends in the direction $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. The halogen ions are solvated in the order $F^- > Cl^- > Br^- > I^-$. Thus, from electrolytic transport methods the smaller the simple ion and the greater its charge, the greater its solvation. Cd^{2+}, Zn^{2+}, and Cu^{2+} ions are highly hydrated. There are a few data for hydration of complex anions. Their hydration numbers are regular except for the SO_4^{2-} ion which is strongly dependent on concentration. Table II shows the same order of alkali metal ion water transport and indicates that for the mixed solvent systems cations are sometimes selectively solvated by the nonaqueous component, while anions are always selectively solvated by the water component. The dynamic type transport methods are the only type in which hydrodynamical solvation is relevant.[92] Transport methods should yield higher solvation numbers than the generally accepted[24,92–99] values, since these methods measure both hydrodynamical solvation and primary and secondary solvation types. Hydrogen and hydroxyl ions were exceptions and gave smaller hydration numbers (*e.g.*, $H^+ = 1–5$) by transport experiments than by other methods (*e.g.*, $H^+ > 13$). The Grotthus transport method of conduction of these ions results in low solvation numbers.

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B. CONDUCTANCE

1. Theoretical

Solvation numbers of ions can be calculated from electrolytic conductance data using the Stokes ionic radii, r_s, from the limiting ionic conductances at infinite dilution, λ_0, obtained from the limiting conductance of electrolytes and the limiting conductance of the standard reference perchlorate ion[100,101] as follows. For the tetraalkylammonium salts in benzene and sulfolane,[100,102] the λ_0 increase from ethyl to methyl substituent was lower than expected. Analogous to the behavior of nitrobenzene solutions, the small increase of the limiting conductance in sulfolane was explained as an interaction between the tetramethylammonium charge and solvent molecule dipoles.

The Stokes ionic radii, r_s, were calculated from the λ_0 values of unsolvated Et_4N^+, Pr_4N^+, and Bu_4N^+ applying the equation

$$r_s = 0.82|z|/\lambda_0\eta_0 \qquad (13)$$

and the Robinson and Stokes correction factors r_0/r_s were calculated[103] using the crystallographic radii r_s. From linear plots of r_0/r_s *vs.* r_s, the correction factors of the alkali metal ions were calculated since the corresponding r_s values were between or near those of the tetraalkylammonium ions. From the plot the correct radii, r_{cor}, of the solvated ions were found, and the volumes of the solvation shells were obtained from the equation

$$V = \frac{4}{3}\pi(r_{cor}^3 - r_0^3) \qquad (14)$$

Assuming negligible contraction because of electrostriction of the solvent sulfolane next to the ions, the number of molecules in the solvodynamic unit was calculated from the molecular volume of sulfolane (158 Å^3).

The lowest values for the solvation numbers of cations occur in solvents with the greatest molecular volumes as sulfolane and nitrobenzene.

The above procedure yielded[104] an effective hydrated radius for ions with a Stokes radius greater than 2.5 Å. The procedure was applied to ions of smaller Stokes radii assuming that all tetraalkylammonium ions, except the tetramethylammonium ion, were unhydrated and defining the effective ionic hydrated radius, r_H, by a calibration curve which possessed a finite limit as the Stokes radii, r_s, went to zero. The curve was a plot of the crystal radii, r_0, versus r_s for the tetraalkylammonium ions, except for the tetramethylammonium ion. From this curve one can evaluate the deviations from the Stokes' law radius and the necessary corrections thereto. This method yielded the hydration numbers of the lanthanide ions from conductance data.[105,106]

Ulich[107] calculated solvation numbers of ions from the Stokes' law radii from conductance and the radius proper of the ions.

2. Experimental Techniques

In conductance methods for ion solvation the conductances of electrolytes at different concentrations are obtained at a given temperature. The equivalent conductance as a function of concentration is extrapolated to yield the equivalent conductance of the electrolyte, Λ_0, at infinite dilution. Λ_0 is split into the equivalent conductances of the ions, λ_0^{+n} and λ_0^{-m}, using transference data extrapolated to infinite dilution or by assuming a limiting conductance for a standard reference ion.[100,101] Here n and m are the valences of the ions. Using the limiting ionic conductances, the crystalline radii, and the molecular volumes of the solvents, the solvation numbers of the ions are calculated as shown in the theoretical section.

3. Solvation Numbers Determined

In Table IV solvation numbers of ions are presented.

Accepting electrolytic conduction in solution as due mainly to electrolytic transport and that electroosmotic effects contribute negligibly, the absolute hydrations of the ions listed in Table IV were calculated from the electrolytic transport of water by alkali chloride and bromide.[108] Both static and dynamic solvation were postulated.

Data[109] on the conductance of alkali and alkaline earth metals show a relatively large increase of equivalent conductance with dilution corresponding to greater hydration. The greater the electrical charge density of an ion, the smaller are its hydration and viscosity effect.

In methyl ethyl ketone and in acetone at 25°, the electrical conductances of numerous electrolytes were measured.[110] The conductance of tetraethylammonium picrate was also determined at 0 and 50°. The limiting equivalent conductances were found. The mobilities and solvation numbers were calculated. Extensive conductivity work was done in CH_3CN solvent[111] and the solvation numbers were obtained; see Table IV.

Changes in composition of $CrCl_3$ in H_2O represented by $[Cr(H_2O)_4]Cl_3$ (I) $\rightleftarrows$ $[Cr(H_2O)_5Cl]Cl_2$ (II) $\rightleftarrows$ $[Cr(H_2O)_6]Cl_3$ (III) occurred, but more slowly in 98.5% D_2O.[112]

Conductance measurements showed[113] that Li^+ is much more highly hydrated than Na^+ and K^+.

In a partition study, conductance data on the organic phase showed, in general, an average of $4.0H_2O$ per $UO_2(NO_3)_2$ molecule in the cases of ethers, esters, and ketones. Alcohols gave more complex data.[114]

Ion hydration has been found using conductivity[115] to be high even at a temperature of 340°.

Conductivity studies at 25° on lithium nitrate showed that the ion-size parameter *A* increased progressively in going from water to ethanol.[116] This was attributed to change in solva-

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Table IV

Solvation Numbers of Ions from Conductivity

Solvent	*Temp, °C*	*Ion*	*Solvation no.*	*Ref*	*Solvent*	*Temp, °C*	*Ion*	*Solvation no.*	*Ref*
Sulfolane	30	Li$^+$	1.4	100	Methanol	25	Li$^+$	7	110
Sulfolane	30	Na$^+$	2.0	100	Methanol	25	Na$^+$	5-6	110
Sulfolane	30	K$^+$	1.5	100	Methanol	25	K$^+$	4	110
Sulfolane	30	Pb$^+$	1.4	100	Methanol	25	Cl$^-$	4	110
Sulfolane	30	Cs$^+$	1.3	100	Methanol	25	Br$^-$	3	110
Sulfolane	30	NH$_4^+$	0.9	100	Methanol	25	I$^-$	1	110
Sulfolane	30	Cl$^-$	~0	100	Methanol	25	Pi$^-$	0	110
Sulfolane	30	Br$^-$	~0	100	Ethanol	25	Li$^+$	6	110
Sulfolane	30	I$^-$	~0	100	Ethanol	25	Na$^+$	4	110
Sulfolane	30	ClO$_4^-$	~0	100	Ethanol	25	K$^+$	3-4	110
Water	25	La^{3+} to Nd^{3+}	12.8 ± 0.1	105, 106	Ethanol	25	Cl$^-$	4	110
					Ethanol	25	Br$^-$	4	110
Water	25	Dy^{3+} to Yb^{3+}	13.9 ± 0.1	105, 106	Ethanol	25	I$^-$	2	110
					Ethanol	25	Pi$^-$	0	110
Water	25	Sm^{3+}	13.1	105	Acetone	25	Li$^+$	5	110
Water	25	Eu^{3+}	13.3	105	Acetone	25	Na$^+$	4-5	110
Water	25	Gd^{3+}	13.4	107	Acetone	25	K$^+$	4	110
Water	25	Li$^+$	6-7	107	Acetone	25	Cl$^-$	2	110
Water	25	Na$^+$	2-4	107	Acetone	25	Br$^-$	1	110
Methanol	25	Li$^+$	7	107	Acetone	25	I$^-$	0-1	110
Methanol	25	Na$^+$	5-6	107	Acetone	25	Pi$^-$	0	110
Methanol	25	K$^+$	4	107	Methyl ethyl ketone	25	Li$^+$	4	110
Methanol	25	Cl	4	107	Methyl ethyl ketone	25	Na$^+$	3	110
Methanol	25	Br$^-$	2-3	107	Methyl ethyl ketone	25	K$^+$	2	110
Methanol	25	I$^-$	0-3	107	Methyl ethyl ketone	25	Cl$^-$	2	110
Ethanol	25	Li$^+$	6	107	Methyl ethyl ketone	25	Br$^-$	1	110
Ethanol	25	Na$^+$	4-5	107	Methyl ethyl ketone	25	I$^-$	0-1	110
Ethanol	25	K$^+$	3-4	107	Methyl ethyl ketone	25	Pi$^-$	0	110
Ethanol	25	Cl$^-$	4-5	107	Acetonitrile	25	Li$^+$	9	110
Ethanol	25	Br$^-$	4	107	Acetonitrile	25	Na$^+$	6	110
Ethanol	25	I$^-$	2-3	107	Acetonitrile	25	K$^+$	3	110
Acetone	25	Li$^+$	4	107	Acetonitrile	25	Cl$^-$	2	110
Acetone	25	Na$^+$	4-5	107	Acetonitrile	25	Br$^-$	1-2	110
Acetone	25	K$^+$	4	107	Acetonitrile	25	I$^-$	0-1	110
Acetone	25	Cl$^-$	2	107	Acetonitrile	25	Pi$^-$	0	110
Acetone	25	Br$^-$	1	107	Methylamine	25	Cl$^-$	1	110
Acetone	25	I$^-$	0-1	107	Methylamine	25	I$^-$	1	110
Acetonitrile	25	Na$^+$	5	107	Methylamine	25	Pi$^-$	0	110
Acetonitrile	25	K$^+$	3-4	107	Ethylene chloride	25	Cl$^-$	2	110
Acetonitrile	25	Br$^-$	1-3	107	Ethylene chloride	25	I$^-$	0-1	110
Acetonitrile	25	I$^-$	0-2	107	Ethylene chloride	25	Pi$^-$	0	110
Furfural	25	Na$^+$	5	107	Water		Li$^+$	21	123
Furfural	25	K$^+$	4	107	Water		Na$^+$	10	123
Furfural	25	I$^-$	0-1	107	Water		K$^+$	7	123
Pyridine	25	Na$^+$	4	107	Formamide	25	Li$^+$	5.4	135
Pyridine	25	K$^+$	2-3	107	Formamide	25	Na$^+$	4.0	135
Pyridine	25	I$^-$	0-1	107	Formamide	25	K$^+$	2.5	135
Water		Li$^+$	14	108	Formamide	25	Rb$^+$	2.3	135
Water		Na$^+$	9	108	Formamide	25	Cs$^+$	1.9	135
Water		K$^+$	5	108	Formamide	25	H$^+$	3.5	135
Water		Cl$^-$	4	108	Water	25	Li$^+$	7.0	136
Water		Br$^-$	3	108	Water	25	Na$^+$	5.0	136

tion of lithium ion from water to alcohol molecules. Nitrate ion was also found to solvate to some extent at least in alcohol.

From conductivity measurements in the H_2O–H_2O_2 system, it was concluded[117] that in pure H_2O_2 the solvation of the alkali metal cations decreases in the order Li > Na > K > Rb > Cs.

Plots of conductance of solutions against temperature were found to show breaks at the temperatures corresponding to the changes in the states of hydration.[118] The salts, the number of water moles per mole of salt below and above the temperature, and the temperature were given in the above order for each salt studied: thus, $CoCl_2$, 6, 2, 48°; Na_2CO_3, 7, 1, 35°; $Sr(NO_3)_2$, 4, 0, 31°; Na_2SO_4, 7, 0, 34°; NaBr, 2, 0, 50.5°;

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Na_2CrO_4, 4, 0, 67.5°. In the case of phase changes no breaks in the curves were found.

Differences in apparent degrees of ionization of electrolytes from boiling point, freezing point, and conductivity were explained in terms of, among other things, primary ion hydration.[119]

Electrical conductances and viscosities of solutions of mixed electrolytes lower than the means of the single salt values at the same total molarity were discussed in terms of ion hydration and dielectric constant.[120]

Electrical conductivity *vs.* temperature plots for saturated solutions of electrolytes gave two straight lines, the extrapolation of which intersected at the transition temperature of the two hydrates.[121] Such plots for $CoSO_4 \cdot 6H_2O$ saturated at 60° and for $MgSO_4$ were linear and without any break at the transition temperature, perhaps owing to metastable higher hydrates of these salts.

The limiting conductance of LiBr in SO_2 at 0.22° indicated that Li^+ and K^+ ions are impeded comparably in their association with bromide ion due to solvation of the cations[122] by the anions penetrating the solvation sheaths of the Li^+ and K^+ ions. Countercurrent migration was used to obtain hydration numbers of some alkali metal ions[123] (see Table IV).

From conductance data, it was found that in ethanol strong solvation results with large ions obeying Walden's rule, but in water deviations arose from the change in the ion size with temperature due to difference in solvation.[124]

From conductance data in dimethylformamide (DMFA) and in DMFA–H_2O mixtures, found or inferred were $MgCl_2 \cdot 6DMFA$, $MgBr_2 \cdot 6DMFA$, $MgCl_2 \cdot 3DMFA$, $MgCl_2 \cdot 4DMFA \cdot 2H_2O$, $MgCl_2 \cdot 3DMFA \cdot 3H_2O$, and $MgCl_2 \cdot 2DMFA \cdot 4H_2O$.[125]

Conductance data at 35° in dioxane–water mixtures showed that the solvation of K^+ and Na^+ varies alike in 10 and 20% dioxane solutions. In 30% dioxane solutions, polarizing powers for dioxane and for water molecules in the solvation sphere differ, and the preference of a particular ion for one solvent species is evident.[126,127]

From conductivity data on UO_2^{2+} in solvents ranging in dielectric constant from 7 to 109,[128] solvation was isoergic in several solvents, and water and organic molecules competed in the primary solvation shell. In strongly polar solvents, water in the shell was completely replaced by the solvent which formed a complex with the UO_2^{2+}.

Surface conduction of NaCl showed that the low conductance was through adsorbed semihydrated ions, since hexanol did not decrease the conductance.[129] Higher conductance samples were affected by hexanol, perhaps owing to conduction in grooves. From the mass action law, the average number of H_2O molecules of semihydrated cations and anions was 3 at low humidities and about 10 at high humidities. The ten molecules corresponded to a second hydration shell.

Conductance data at 0.02° indicated a smaller solvation of free Na^+ in SO_2 than in several other solvents.[130] In mobility behavior in SO_2, Na^+ resembles K^+ more than Li^+.

Selective solvations in asymmetric solvents were studied by conductivity measurements.[131] A study of conductance data in protic and aprotic solvents indicated the role of the protons in enhancing the solvation of anions, but the very secondary effect of protons on the solvation of cations solvated by ion–dipolar interaction.[132]

From conductance measurements on aqueous solutions, it was found that hydrostatic pressure reduced the radii of the hydrated ions until above 2000 kg/m^2 the hydration atmosphere was stripped to the innermost solvation sheaths of strongly bound water.[133]

Conductance measurements at 25° in tetrahydrofuran (THF) of tetraphenylborides of several cations from 10^{-6} to 2×10^{-4} *M* were made and the limiting conductances obtained from the extrapolation.[134] The limiting conductance of the cations were found by assuming $\lambda_0^+[(\text{isoamyl})_3\text{BuN}^+] = \lambda_0^-[\text{BPh}_4^-]$. The lowest value of λ_0^+ was found for the assumedly most solvated Li^+ and the largest λ_0^+ for the assumedly unsolvated Cs^+. The tetraalkylammonium ions were found to be unsolvated.

Limiting values of moving boundary transference numbers at 25° were obtained for the ions of KCl using formamide and formamide–water as the solvents.[135] The numbers were combined with equivalent conductance data to give limiting ionic conductances in formamide. From these ionic solvation numbers were calculated[136] ignoring any electrostrictive contraction of the solvent molecules next to the ions (see Table IV).

Conductance measurements of aqueous solutions of KCl and LiCl mixed with glycine or urea showed that the mechanism and state of hydration of the ions and solutes were the same in mixed solutions and water.[137]

Agreement was found among four methods (three involving conductance) of estimating the total hydration atmosphere or water-structure-enhanced regions surrounding the alkali metal cations.[138] For Na^+ the number of water molecules in the total atmosphere approximates closely the number in the Frank–Wen cluster in pure water at the same temperatures.

4. *Significance*

Conductance data add to the varieties of solvents and ions investigated with respect to solvation. The variation of solvation number for a given ion with solvent is evident. Thus, at 25° the solvation number of K^+ varies from 1.5 in sulfolane

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to 7 in formamide. The data indicate that in all solvents the solvation of the alkali metals is in the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$, except in acetone where the solvation of Li^+, Na^+, and K^+ is about the same.[107] The order of solvation of the halogen ions in all solvents is, in general, $Cl^- > Br^- > I^-$, though in methylamine at 25° Cl^- and I^- ions have the same solvation numbers.

From conductance limiting solvation numbers are obtained since limiting values of the equivalent conductance of the ions are used in the calculations. These numbers are relative to some chosen ion since the limiting equivalent conductances of ions are relative to some standard reference ion as perchlorate ion. Using this method, the results of different workers under similar conditions seem consistent. Refer to solvation numbers in methanol and ethanol (Table IV) from ref 107 and 110.

C. ELECTROMOTIVE FORCE

1. Theory

Electromotive force data gave the solvation number of HCl[139] and, provided the solvation number of one ion was assumed from some other source, gave the solvation number of the other ion. The Hudson–Saville[140] approach to ionic solvation in liquid mixtures was used and was similar to that of Robinson and Stokes[141] and of Glueckauf[142] in the case of concentrated aqueous solutions.

The Born equation, which depends on the potential of a charged sphere in a uniform dielectric, cannot be applied accurately to an ion in solution since the ion is comparable in dimensions to the solvent molecules. Near-dielectric saturation prevails close to the ion. The first layer of solvent molecules considered as completely orientated can be treated as a firmly bound ionic solvation shell, the formation of which as the gaseous ion enters the solution will cause a loss of free energy by the coordinated water molecules. The Born-type equation could be used to calculate the remaining free energy change assumed to be relatively small especially in solutions of high dielectric constants. Also, the ions were assumed to be preferentially solvated by the more polar water molecules, particularly when the water content was high.

The coordination of n water molecules, when 1 mol of HCl as ions dissolve from the gas state to a standard state in aqueous solution, was written[1]

$$(\mathrm{H} + \mathrm{Cl})_{\mathrm{gas}} + n\mathrm{W}_1 \rightleftarrows (\mathrm{H} + \mathrm{Cl}), n\mathrm{W} \qquad (15)$$

where H^+ and Cl^- ions are written without their charges and W stands for water. The free energy change for the process was

$$\Delta G^{\mathrm{W}} = \mu^{\mathrm{W}}{}_{(\mathrm{H+Cl}),n\mathrm{W}} - \mu_{(\mathrm{H+Cl})} - n\mu^{\mathrm{W}}{}_{\mathrm{W}} \qquad (16)$$

For the same process in an organic solvent–water mixture, the free energy change was

$$\Delta G^{\mathrm{S}} = \mu^{\mathrm{S}}{}_{(\mathrm{H+Cl}),n\mathrm{W}} - \mu_{(\mathrm{H+Cl})} - n\mu^{\mathrm{S}}{}_{\mathrm{W}} \qquad (17)$$

Consider the difference

$$\Delta G = \mu^{\mathrm{S}}{}_{(\mathrm{H+Cl}),n\mathrm{W}} - \mu^{\mathrm{W}}{}_{(\mathrm{H+Cl}),n\mathrm{W}} \qquad (18)$$

Assuming negligible interaction of the solvated ions with the solvent, the difference in the partial molal free energies of the solvated ions in the two solvents depends only on the difference in the concentrations of the ions in the two. This term was taken as zero when the standard state was either the mole fraction or the molar one. Neither scale probably made the assumption exactly true. Thus

$$\mu^{\mathrm{S}}{}_{(\mathrm{H+Cl}),n\mathrm{W}} = \mu^{\mathrm{W}}{}_{(\mathrm{H+Cl}),n\mathrm{W}} \qquad (19)$$

Hence

$$\Delta G^{\mathrm{S}} - \Delta G^{\mathrm{W}} = n(\mu^{\mathrm{W}}{}_{\mathrm{W}} - \mu^{\mathrm{S}}{}_{\mathrm{W}}) = -F({}^{\mathrm{S}}E^\circ - E^\circ) \qquad (20)$$

For the water in the mixture, the partial molal free energy was expressed in terms of mole fraction or of volume fraction statistics, and, for simplicity, expressions were developed for ideal mixtures. If N_{W} is the mole fraction and ϕ_{W} the volume fraction of water, then

$$\mu^{\mathrm{W}}{}_{\mathrm{W}} - \mu^{\mathrm{S}}{}_{\mathrm{W}} = -RT \ln N_{\mathrm{W}} = -RT \ln \phi_{\mathrm{W}} \qquad (21)$$

Now using $E_{\mathrm{N}}°$ for the mole fraction and $E_\phi°$ for the volume fraction models, respectively, we have the equations

$${}^{\mathrm{S}}E_{\mathrm{N}}^\circ = {}^{\mathrm{W}}E_{\mathrm{N}}^\circ + n\frac{RT}{F} \ln N_{\mathrm{W}} \qquad (22)$$

and

$${}^{\mathrm{S}}E_{\mathrm{c}}^\circ = {}^{\mathrm{W}}E_{\mathrm{c}}^\circ + n\frac{RT}{F} \ln \phi_{\mathrm{W}} \qquad (23)$$

Equations 22 and 23 reduce to

$${}^{\mathrm{S}}E_{\mathrm{m}}^\circ = {}^{\mathrm{W}}E_{\mathrm{m}}^\circ + nk \log w + k(n-2) \log \frac{M_{\mathrm{XY}}}{M_{\mathrm{Y}}} \qquad (24)$$

$${}^{\mathrm{S}}E_m^\circ = {}^{\mathrm{W}}E_{\mathrm{m}}^\circ + nk \log w + k(n-2) \log \rho \qquad (25)$$

where w is the weight fraction of water, and ρ is the density. For water-rich solutions, $\log \rho$ and $\log M_{\mathrm{XY}}/M_{\mathrm{Y}}$ are small; and, if n is close to 2, both eq 24 and 25 approximate to

$${}^{\mathrm{S}}E_{\mathrm{m}}^\circ = {}^{\mathrm{W}}E_{\mathrm{m}}^\circ + nk \ln w \qquad (26)$$

Equations 22 and 23 can be used to obtain the solvation number by plotting ${}^{\mathrm{S}}E_{\mathrm{c}}°$ *vs.* $\ln \phi_{\mathrm{W}}$ and plotting ${}^{\mathrm{S}}E_{\mathrm{N}}°$ *vs.* $\ln N_{\mathrm{W}}$. The plot of ${}^{\mathrm{S}}E_{\mathrm{N}}°$ *vs.* $\ln N_{\mathrm{W}}$ showed no striking correlation and was not used.[143]

2. Experimental Technique

From potential measurements in pure and mixed solvents on cells at various concentrations of electrolyte and at fixed temperatures, the standard potential of the cell in each solvent and at each temperature is calculated.[143] The volume fractions of the solvent components are determined from weight and density measurements or from volume measurements. Slopes of the linear plots of ${}^{\mathrm{S}}E_{\mathrm{c}}°$ *vs.* $\ln \phi_{\mathrm{W}}$ yield the solvation number n.

3. Solvation Numbers Determined

For the cell[139]

Pt, H_2 (1 atm)|HCl|AgCl–Ag

the solvation number of HCl was determined to be 2.2. If

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n of one ion could be determined, that of the other ion would be fixed.

From the potential of the proper cell in various mixtures of H_2O–MeCN, the free energy dependence of solvation of Ag^+ ion on the composition of the H_2O–MeCN was determined.[144]

Potentiometry was used to determine the stability conconstants of the 1:1 and 2:1 complexes of Al–1,10-phenanthroline.[145] Other metal complexes of the reagent were also studied.

Observing change of pH with time, hydration and polymerization of various vanadate ions were followed.[146] VO_4^{3-} was protonated in steps much like that for PO_4^{3-}. The H_3VO_4 formed partially hydrated to an equilibrium ratio $V(OH)_5/H_3VO_4 \sim 3$.

Effects of ion hydration and dielectric constant on standard potentials were investigated in H_2O–MeOH, H_2O–EtOH, and H_2O–dioxane solvents.[147] For certain dielectric constant ranges $E°$ was linear with $1/D$. The range broadened with increasing molecular weight of the nonaqueous solvent. Deviations from linearity occurred when the solvents attained 17 mol of water/1000 g of mixed solvent. The deviations were, therefore, related to the loss of coordination water by ions. Solvation of the ions beyond their coordination numbers caused no deviation from linearity of the $E°$ *vs.* $1/D$ plot. $E°$ represents standard potential and D represents the solvent dielectric constant.

Ion solvation in nonaqueous solvents and their aqueous mixtures were studied using electromotive force; and molar free energies of transfer of some halogen acids and alkali chlorides, from water to 10 and 43.12 wt % methanol-water mixtures, were separated into ion constituent values by extrathermodynamic assumptions.[148,149] A structural theory of ion solvation explained the ionic free energy values.

Equations were given[150] for the dependence of the normal potential ($E_N°$, $E_m°$, and $E_c°$) of cells without transference on the dielectric properties of a mixed solvent, primary hydration of an electrolyte, and the cation–anion equilibria. From electromotive force the constants are obtained for the primary hydration numbers (Table V) and transsolvation ($H_2O \rightarrow$ MeOH) equilibria in water for Li^+, Na^+, and K^+.

Table V

Solvation Numbers for Ions from Electromotive Force Data

Solvent	*Ref ion*	*Solvation no. of ref ion*	*Solvated ion*	*Solvation no. of ref ion*	*Ref no.*
Water–methanol	Cl^-	0	Li^+	4 (primary)	152
Water–methanol	Cl^-	0	Na^+	4 (primary)	152
Water–methanol	Cl^-	0	K^+	4 (primary)	152
Water–methanol	Cl^-	0	H^+	1 (primary)	152

Potential studies on galvanic cells showed that in molten salt solutions containing water, water molecules were ligands competing with bromide ions in displacing nitrate ions from the coordination spheres of cadmium ions.[151] Bromide ions displace nitrate ions more readily than water molecules from the coordination sphere since the association constant for the reaction $Cd^{2+} + Br^- \rightarrow CdBr^+$ increased with decreasing water content. The increase measured the tendency of the Cd^{2+} ions to hydrate.

A further study of potential measurements has been made on ion solvation in nonaqueous solvents and their aqueous mixtures, but solvation numbers were not listed.[152]

4. *Significance*

The value of $n = 2.2$ for HCl from cell potential measurement is lower than that from other methods with the exception of diffusion[153] ($u = 2.1$). From activity coefficients, Stokes and Robinson[154] found $n = 8$ and Glueckauf[142] found $n = 4.7$. The ${}^{S}E_N°$ *vs.* $\ln N_W$ plots give higher than 2.2, namely 2.7–5.0.

The electromotive force determination of solvation numbers seems to result in primary shell solvation. From Table V this method shows Li, Na, and K ions are equally hydrated in their primary shells.

D. THERMODYNAMICS

1. *Theoretical and Experimental Data*

Solvation from solvation energies depends on knowing individual ion solvation energies. This knowledge is based on some nonthermodynamic, generally theoretical, principle for a division of the observed thermodynamic function for a binary electrolyte. The principles involve the dependence of the energy on some function of the reciprocal ionic radii.

One attempt at finding individual ionic energies divided the total heat of solvation of K^+F^-, $\Delta H°_{K^+} = \Delta H°_{F^-} = -95.5$ kcal mol^{-1} (adjusted to $\Delta H°_{K^+} = -94$ kcal mol^{-1} and $\Delta H°_{F^-} = -97$ kcal mol^{-1}), to account for the different spatial distribution of the water molecules about the K^+ and F^- ions owing to the noncentral location of the water molecule dipole. Using these values, $\Delta H°_{H^+}$ was found[155] to be -276 kcal mol^{-1}. It was suggested[156–158] that this division of solvation enthalpies was oversimplified and not in keeping with Bernal and Fowler's calculations of enthalpies and free energies of hydration.

The Born equation with empirically corrected radii was used to represent the free energies of the solvation of ions.[159] This is believed[158] less satisfactory than the Bernal and Fowler[155] method.

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The calculations of Eley and Evans,[160] from a comparative study of the methods up to 1953, were selected[156] as the most acceptable for the determination of individual ion hydration heats. The values of $\Delta H°_{K^+}$ and $\Delta H°_{F^-}$ were given as -90 and -91 kcal mol^{-1}, respectively. Verwey[161] split $\Delta H°_{KF}$ into $\Delta H_{K^+} = -75$ and $\Delta H°_{F^-} = -122$ kcal mol^{-1}.

Buckingham[162] proposed a more complete calculation of hydration enthalpy which included terms dealing with ion–dipole, dipole–dipole, ion–quadrupole interactions, and effects of induced moments.

Halliwell and Nyburg[163] obtained $\Delta H°_{H^+}$ using the difference of conventional hydration energies of oppositely charged pairs of ions of the same radii. Absolute and conventional standard enthalpies of hydration for a cation, M, of valence z^+ and for an anion, A, of valence z^- are related by

$$\Delta \bar{H}°_{M^{z+}} = \Delta H°_{M^{z+}} - z^+\Delta H°_{H^+} \tag{27}$$

$$\Delta \bar{H}°_{A^{z-}} = \Delta H°_{A^{z-}} + z^-\Delta H°_{H^+} \tag{28}$$

where the $\Delta\bar{H}°$'s are the conventional relative enthalpies and the $\Delta H°$'s are the absolute ionic enthalpies of the indicated species. Subtracting eq 28 from eq 27 yields for uni-univalent electrolytes

$$\Delta \bar{H}°_{M^{z+}} - \Delta \bar{H}°_{A^{z-}} = [\Delta H°_{M^{z+}} - \Delta H°_{A^{z-}}] - 2\Delta H°_{H^+} \tag{29}$$

Experimental values of conventional heats of hydration have been compiled.[164] These values of $\Delta H_{M^{z+}}$ and $\Delta H_{A^{z-}}$ can be plotted *vs.* some function of the radii[165–167] of cations and anions, respectively, and from these curves a single curve can be plotted for the left-hand side of eq 29 as the same function of ionic radius. The radii used in this latter plot are not necessarily the radii of any particular ions since few cation–anion pairs have identical radii. If the theoretical relationship between the conventional enthalpies of hydration and the inverse function of the radius against which they have been plotted is known, the extrapolation of the left-hand side of eq 29 to infinite radius should ideally yield $2\Delta H°_{H^+}$ as the intercept on the $\Delta H°_{M^{z+}} - \Delta H°_{A^{z-}}$ axis.

Usually no single-powered function of the reciprocal of the hydrated radius, that is, the sum of the radius of the ion and the radius of the water molecule, represents uniquely the heats of hydration of ions[158] because of different dependencies on the radius of the primary shell[156,157,168] and outer region. The former depends principally on r_h^{-2}, where r_h is the hydrated radius; the latter depends on $(r_i + 2r_{H_2O})^{-1}$ where r_i is the radius of the ion and r_{H_2O} that of the water molecule. To obviate this difficulty, the best, self-consistent values of the conventional relative enthalpies, $\Delta\bar{H}°$, for cations and anions were plotted[163] *vs.* $(r_i + r_{H_2O})^{-3}$, where r_{H_2O} was taken as 1.38 Å and r_i's were taken mainly from Pauling[169] and Ahrens.[170] After considering "hard-sphere" and "soft-sphere" ion–solvent contact models and also accounting for a possible coordination number of 4 or 6 in the primary shell, the best value for $\Delta H°_{H^+}$ was chosen as -260.7 ± 2.5 kcal mol^{-1}. The form of the function for large r_h has been criticized;[158] however, the plot of the left-hand side of eq 29 *vs.* $(r_i + r_{H_2O})^{-3}$ has been approved[158] since for cations and anions of the same radii the supposed differences in the heats of solvation apparently[162] arise mainly from the ion–quadripole interaction terms. Verwey's[161] orientation of water at ions may cause an error in the difference plot. Halliwell and Nyburg's difference plot gives a maximum of $\Delta H°_{H^+}$ of about 267 kcal mol^{-1}. High values[171] of -280 or -292 kcal mol^{-1} for free energy[172,173] or -302 kcal mol^{-1} for the enthalpy of hydration of the H^+ is considered unlikely.[158] Other data in the literature are -259 kcal mol^{-1} for free energy,[174] and -265[175] and -263[176] kcal mol^{-1} for enthalpy. The method discussed above perhaps[168] limits the uncertainity in $\Delta H°_{H^+}$ to no more than 7 kcal mol^{-1}.

Work has been done[158,177–179] on the heat and standard free energy of formation in the gaseous state (g) of H_3O^+(g) from H^+(g) and H_2O(g). Thermodynamic cycles involving H_3O^+, ClO_4^- and NH_4^+, ClO_4^- were assigned the same crystal lattice energies since the ions were of the same charge. Proton affinity of water was taken as identical with the enthalpy change for the protonation of water at room temperature. The validity of this assumption was discussed.[158] The values at 298° of $\Delta H°_{H_2O}$ $(-P_{H_2O})$, $\Delta S°_{H_2O}$, and $\Delta F°_{H_2O}$ are recorded[158] as -170, kcal mol$-^1$, -27 eu, and -162 kcal mol^{-1}.

a. Equilibrium Methods

The hydration of gaseous ions was studied.[180–184] Hydrogen ions were investigated[184] in irradiated water vapor from 0.1 to 6 Torr and from 5 to 600°. The equilibrium constants $K_{(n-1),n}$ were calculated from the concentration of the species $A^+ \cdot n$S, where the ion A^+ is produced by some form of ionizing radiation or thermal means, and mass spectrometric measurements were made of the relative concentrations of the species A^+S_n, A^+S_{n-1}, $B^- \cdot S_n$, $B^- \cdot S_{n-1}$, where A^+ and B^- are positive and negative ions and S is a solvent molecule. In the equilibrium expression

$$K_{(n-1),n} = \frac{P_{A^+ \cdot nS}}{P_{A^+ \cdot (n-1)S}P_S} \tag{30}$$

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the equilibrium pressures were substituted by the ratio of the ion mass-spectrometric intensities of the corresponding ions. From the equilibrium constants the stepwise free energies $\Delta G°_{n-1,n}$, $\Delta H°_{n-1,n}$, $\Delta S°_{n-1,n}$ were determined for the processes

$$A^+ + S \rightleftarrows A^+{\cdot}S \quad (0, 1) \tag{31}$$

$$A^+{\cdot}S + S \rightleftarrows A^+{\cdot}2S \quad (1, 2) \tag{32}$$

$$A^+{\cdot}(n-1)S + S \rightleftarrows A^+{\cdot}nS \quad ((n-1), n) \tag{33}$$

For hydrogen ion studies H_2O^+ and OH^+ ions were produced by irradiation of water vapor by electrons, protons, and α particles. These ions react rapidly[185–187] with water vapor to produce H_3O^+, which in turn reacts with water vapor producing hydrates as shown in Table VI. The hydration reactions are exothermic and a third body would be necessary in eq 32 and 33.

Enthalpies $\Delta H_{n-1,n}$, the enthalpies for the hydration of the $H^+{\cdot}(n-1)H_2O$ ion to $H^+{\cdot}nH_2O$ ion, were compared with values of $Na^+{\cdot}nH_2O$ in the literature.[188] It was found, assuming the radius of the central H_3O^+ ion was similar to Na^+ ion, that $\Delta H_{0,4}$ and ΔH_{0-6} for the Na^+ ion which were -104 and -114, respectively, compared favorably with $\Delta H_{1,5}$ and $\Delta H_{1,7}$ for H_3O^+ which were -91 and -115. From the heat of solvation of the proton in liquid water,[168,174] -261 kcal mol^{-1}, and the enthalpy, $\Delta H_1 = \Delta H_{0,8} + 8\Delta H_{\text{evap}}(H_2O) - 213$ kcal/mol^{-1}, the heat of solvation of $H^+(H_2O)_8(g)$ into liquid water (-48 kcal mol^{-1}) was found from the difference. Thus these data verify the solvation numbers for Na^+ given in Table VI.

Solubility[189] data suggest that NaCl solutions consist of $NaCl{\cdot}2H_2O$ aggregates separated by water. Added HCl removes ten water molecules per HCl molecule and reduces the solubility of NaCl. If the number of water molecules is reduced so that they are not numerous enough to separate the aggregates, the latter combine and precipitate.

The entropy of neutralization of HCl can be calculated assuming that the ten water molecules surrounding each HCl is composed of two layers of five molecules each, and that two of the water molecules in the outside layer are replaced by two NaOH molecules. Thus of the ten water molecules, there is the replacement of two adjacent molecules among five. The replacement can be accomplished in ten ways, giving an entropy

$$\Delta S = 10R \ln 10 = 46 \text{ eu} \tag{34}$$

which agrees well with the value calculated from the heat of neutralization at 18° which is 13,800 cal mol^{-1}, or 47 eu mol^{-1}, neglecting the change in heat content and the corresponding entropy change.

The methods in the preceding two paragraphs deal with solvation numbers of the electrolyte as a whole. Solvation numbers can be found[190] from the entropy decrease when gaseous ions are dissolved in infinitely dilute solutions. The entropy decrease can be calculated from the observed heat effects, and is caused by the free solvent molecules entering into tightly held solvation sheaths. If it is assumed that this decrease equals the change in entropy when free water becomes bound as water of crystallization, the entropy of dissolution of an ion can be used to calculate its hydration number.

Multiply charged or small, singly charged ions increase the viscosity of water and decrease the translational motion of the water molecules nearest them, while large, singly charged ions decrease the viscosity of water and increase the translational motion of water molecules nearest them.[191] This decrease in viscosity is termed negative viscosity. Since the water molecules near the ions are more mobile than in pure water, and since these molecules exchange more frequently than water molecules near other molecules in water, this phenomenon is termed "negative hydration." The ions which exhibit negative hydration also lower the structural temperature of water.

There is a qualitative dependence of the activity coefficient of water on ion hydration,[191] as shown by data that negatively hydrated cations are associated with activity coefficients of water greater than one over a considerable concentration of electrolyte. However, the activity coefficients of water in hydrated cation solutions are less than one except for a relatively small region at lower concentrations.

b. Thermochemical Method for Coordination Numbers

A thermochemical method for estimating the coordination number of an ion in dilute solutions, that is, for obtaining the average number of constantly exchanging water molecules which form the immediate surroundings of the ion, was devised.[192–196] In this method the integral heats of solution of salts in water and in aqueous solutions of acids of various concentrations are measured. The integral heats of solution of a constant concentration of salt in different concentrations of acid were used in calculating the coordination numbers of the ions in dilute solutions. The differences in the heats of solution of anhydrous and of hydrated salts were taken as the heats of hydration of the anhydrous salts.

The protons from the acid and the proton charge were considered to be statistically distributed over the water molecules so that each water molecule became an ion with the average electronic charge and the average protons per ion of ϵ/e, where ϵ is the average positive charge per ion and e is the electronic charge. The formula of the ions from water was $H_{2+(\epsilon/e)}O^{(\epsilon/e)+}$. The Coulombic interaction energies between these ions and cations and anions are, respectively

$$E_k = -n_k\epsilon e/R_k \tag{35}$$

and

$$E_a = n_a\epsilon e/R_a \tag{36}$$

where R_k and R_a are the distances between the charges of water ions in the first coordination spheres and the centers

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of cations and anions, respectively, and n_k and n_a are the coordination numbers of the cations and anions, respectively. The minus sign indicates repulsion (reduction of exothermic heat of solution) between positive ions. If R_k is taken as r_k + 1.38 Å and R_a is r_a + 1.38 Å when r is the crystal radius of an ion, and if $\epsilon = km$, then eq 35 and 36 become, respectively

$$E_k = -\frac{n_k kme}{r_k + 1.38} \times 10^8 \qquad (37a)$$

and

$$E_a = \frac{n_a kme}{r_a + 1.38} \times 10^8 \qquad (38a)$$

The units of the r's are now centimeters and the energies are in ergs per ion. The sum of the two energies multiplied by Avogadro's number and by the factor for converting ergs to calories (2.389 × 10^{-8}), and setting $K = 2.389Nek$ gives

$$E = -K\left(\frac{n_k}{r_k + 1.38} - \frac{n_a}{r_a + 1.38}\right)m \qquad (37b)$$

where E, in calories per mole of salt, is greater than zero.

The integral heat of solution L of the salt in m molal HCl is

$$L = L_0 - K\left(\frac{n_k}{r_k + 1.38} - \frac{n_a}{r_a + 1.38}\right)m \qquad (38b)$$

where L_0 is the integral heat of solution of salt to the same concentration in pure water. Therefore

$$\beta = -\frac{\Delta L}{\Delta m} = K\left(\frac{n_k}{r_k + 1.38} - \frac{n_a}{r_a + 1.38}\right) \qquad (39)$$

The difference between two salts with the same anion but different cation from eq 39 is

$$\beta_1 - \beta_2 = K\left(\frac{n_{k_1}}{r_{k_1} + 1.38} - \frac{n_{k_2}}{r_{k_2} + 1.38}\right) \qquad (40)$$

For a biunivalent salt a factor of 2 is introduced into eq 39 and 40 and a factor of $\beta^1 = \beta/2$ is used. The values of $\beta = \delta_k - \delta_a$, where

$$\delta_k = K\frac{n_k}{r_k + 1.38}; \quad \delta_a = K\frac{n_a}{r_a + 1.38} \qquad (41)$$

These do not change for various valence types of salts if β^1 is used for β. If K can be found so can the coordination numbers of ions from eq 39 and 40. Thus the relation of coordination number to hydration was considered.

Coordination numbers are not directly related to individual ion hydration numbers. The surface density, ρ', of packing of water molecules in the first coordination layer of ions is directly associated with hydration and must be determined. If n is the ion coordination number, r its radius, and $4\pi(r + 1.38)^2$ the area of the first coordination sphere in Å², then

$$\rho' = \frac{n}{4\pi(r + 1.38)^2} \qquad (42)$$

ρ' for the water molecule in water is

$$\rho'_{H_2O} = \frac{n_{H_2O}}{4\pi R^2} \qquad (43)$$

where n_{H_2O} is the average coordination number of water molecules and R is the distance between centers of neighboring water molecules in water. Using X-rays, $n_{H_2O} = 4.6$ and R = 2.90 Å were found.[197] Hence ρ'_{H_2O} = 0.044 Å.

Hydrated ions such as Na^+, $\Delta E > 0$, by weakening the translational motion of nearest water molecules reduce the frequency of their activated jumps compared to that in pure water. For such ions

$$\rho' > \rho'_{H_2O} \qquad (44)$$

Ions such as K^+, Cl^-, Br^-, and I^-, showing negative hydration, have $\Delta E < 0$, and increase, compared to pure water, the frequency of activated jumps of neighboring molecules. For these ions

$$\rho' < \rho'_{H_2O} \qquad (45)$$

Inequalities 44 and 45 permit the estimation of the lower limits for the coordination numbers of hydrated ions and the upper limits for negatively hydrated ions. Thus, $n_{Na^+} > 3.05$, $n_{K^+} > 3.05$, $n_{K^+} < 4.02$, and $n_{Cl^-} < 5.57$. Distinguishing between hydrated and nonhydrated ions (negative hydration), limiting values for coordination numbers can be estimated.

The lower limit for K in eq 39 and 40 was found[191] from β values for NaCl and NaBr ($NaBr \cdot 2H_2O$). From eq 39 for NaCl, the corresponding equation for NaBr was subtracted, giving

$$K\left(\frac{n_{Br^-}}{3.34} - \frac{n_{Cl^-}}{3.19}\right) = 68 \qquad (46)$$

when r_{Br^-} + 1.38 Å = 3.34, r_{Cl^-} + 1.38 Å = 3.19, and $\beta_{NaCl} - \beta_{NaBr} = 210 - 142 = 68$. From eq 46 since $K > 0$, $n_{Br^-} > n_{Cl^-}$. From heats of hydration and also from certain properties of Cl^-, Br^-, and I^- ions, presumably negative hydration increases in this sequence; and, therefore, $\rho'_{Br^-} < \rho'_{Cl^-}$. Hence

$$\frac{n_{Br^-}}{4\pi(3.34)^2} < \frac{n_{Cl^-}}{4\pi(3.19)^2} \qquad (47)$$

and $n_{Br^-} < 1.096 n_{Cl^-}$. Substituting this value of n_{Br^-} into eq 46 yields

$$K\left(\frac{1.096 n_{Cl^-}}{3.34} - \frac{n_{Cl^-}}{3.19}\right) > 68 \qquad (48)$$

or

$$K > 68/0.0147 n_{Cl^-} \qquad (49)$$

Substituting the upper limit for n_{Cl^-} into eq 49 gives the lower limit of K. The equation for KCl

$$K\left(\frac{n_{K^+}}{2.71} + \frac{n_{Cl^-}}{3.19}\right) = 11 \qquad (50)$$

was used. Here $r_{K^+} + 1.38 = 2.71$, $r_{Cl^-} + 1.38 = 3.19$, and 11 is the experimental value of β for KCl. Since β and K are positive

$$\left(\frac{n_{K^+}}{2.71} - \frac{n_{Cl^+}}{3.19}\right) > 0 \qquad (51)$$

It was shown that $n_{K^+} < 4.02$ and hence $n_{Cl^-} < 4.74$. This is smaller than $n_{Cl^-} < 5.57$ obtained from the inequality $\rho'_{Cl^-} < \rho'_{H_2O}$. Substituting $n_{Cl^-} = 4.74$ in eq 49 yields $K > 976$.

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Table VI

Solvation of Various Ions by Different Thermodynamic Methods

Method[a]	*Solvent*	*Ref ion*	*Assumed solvn no. of ref ion*	*Solvated ion*	*Solvn no. of ion*	*Concn of electrolyte, m*[b]	*Phase*	*Temp, °C*	*Ref*
E	Water			H^+	1		Gas	15–600	184
E	Water			H^+	2		Gas	15–600	184
E	Water			H^+	3		Gas	15–600	184
E	Water			H^+	4		Gas	15–600	184
E	Water			H^+	5		Gas	15–600	184
E	Water			H^+	6		Gas	15–600	184
E	Water			H^+	7		Gas	15–600	184
E	Water			H^+	8		Gas	15–600	184
E	Water			Na^+	4		Gas	15–600	184
E	Water			Na^+	6		Gas	15–600	184
IH	Water			Cs^+	0.031		Solution		201
IH	Water			NH_4^+	0.042		Solution		201
IH	Water			Li^+	0.065		Solution		210
IH	Water			Na^+	0.053		Solution		210
AC	Water	Cs^+	0	Rb^+	0	1			217
AC	Water	Cs^+	0	NH_4^+	0.2	1			217
AC	Water	Cs^+	0	K^+	0.6	1			217
AC	Water	Cs^+	0	Li^+	3.4	1			217
AC	Water	Cs^+	0	H^+	3.9	1			217
AC	Water	Cs^+	0	Ba^{2+}	3.0	0.7			217
AC	Water	Cs^+	0	Sr^{2+}	3.7	0.7			217
AC	Water	Cs^+	0	Ca^{2+}	4.3	0.7			217
AC	Water	Cs^+	0	Mg^{2+}	5.1	0.7			217
AC	Water	Cs^+	0	Zn^{2+}	5.3	0.7			217
AC	Water	Cs^+	0	UO_2^{2+}	7.35	0.7			217
AC	Water	Cs^+	0	La^{3+}	7.5	0.7			217
AC	Water	Cs^+	0	Al^{3+}	11.9	0.7			217
AC	Water	Cs^+	0	NO_3^-	0	1			217
AC	Water	Cs^+	0	ClO_4^-	0.3	1			217
AC	Water	Cs^+	0	Cl^-	0.9	1			217
AC	Water	Cs^+	0	Br^-	0.9	1			217
AC	Water	Cs^+	0	I^-	0.9	1			217
AC	Water	Cs^+	0	RSO_3^-	0.9	1			217
AC	Water	Cs^+	0	F^-	1.8	1			217
AC	Water	Cs^+	0	$C_2H_3O_2^-$	2.6	1			217
AC	Water	Cs^+	0	OH^-	4.0	1			217
AC	Water	Cl^-	0	H^+	8	0.01–1.0		25	216
AC	Water	Br^-	0	H^+	8.6	0.1–1.0		25	216
AC	Water	I^-	0	H^+	10.6	0.1–0.7		25	216
AC	Water	ClO_4^-	0	H^+	7.4	0.1–2.0		25	216
AC	Water	Cl^-	0	Li^+	7.1	0.1–1.0		25	216
AC	Water	Br^-	0	Li^+	7.6	0.1–1.5		25	216
AC	Water	I^-	0	Li^+	9.0	0.1–1.0		25	216
AC	Water	ClO_4^-	0	Li^+	8.7	0.2–1.0		25	216
AC	Water	Cl^-	0	Na^+	3.5	0.1–5.0		25	216
AC	Water	Br^-	0	Na^+	4.2	0.1–4.0		25	216
AC	Water	I^-	0	Na^+	5.5	0.1–1.5		25	216
AC	Water	ClO_4^-	0	Na^+	2.1	0.2–4.0		25	216
AC	Water	Cl^-	0	K^+	1.9	0.1–4.0		25	216
AC	Water	Br^-	0	K^+	2.1	0.1–4.0		25	216
AC	Water	I^-	0	K^+	2.5	0.1–4.0		25	216
AC	Water	Cl^-	0	Rb^+	1.2	0.1–1.5		25	216
AC	Water	Br^-	0	Rb^+	0.9	0.1–1.5		25	216
AC	Water	I^-	0	Rb^+	0.6	0.1–1.5		25	216
AC	Water	Cl^-	0	Mg^{2+}	13.7	0.1–1.4		25	216
AC	Water	Br^-	0	Mg^{2+}	17.0	0.1–1.0		25	216
AC	Water	I^-	0	Mg^{2+}	19.0	0.1–0.7		25	216
AC	Water	Cl^-	0	Ca^{2+}	12.0	0.1–1.4		25	216
AC	Water	Br^-	0	Ca^{2+}	14.6	0.1–1.0		25	216
AC	Water	I^-	0	Ca^{2+}	17.0	0.1–0.7		25	216
AC	Water	Cl^-	0	Sr^{2+}	10.7	0.1–1.8		25	216
AC	Water	Br^-	0	Sr^{2+}	12.7	0.1–1.4		25	216
AC	Water	I^-	0	Sr^{2+}	15.5	0.1–1.0		25	216

Table VI (Continued)

Method[a]	*Solvent*	*Ref ion*	*Assumed solvn no. of ref ion*	*Solvated ion*	*Solvn no. of ion*	*Concn o electrolyte, m*[b]	*Phase*	*Temp, °C*	*Ref*
AC	Water	Cl^-	0	Ba^{2+}	7.7	0.1–1.8		25	216
AC	Water	Br^-	0	Ba^{2+}	10.7	0.1–1.5		25	216
AC	Water	I^-	0	Ba^{2+}	15.0	0.1–1.0		25	216
AC	Water	Cl^-	0	Mn^{2+}	11.0	0.1–1.4		25	216
AC	Water	Cl^-	0	Fe^{2+}	12.0	0.1–1.4		25	216
AC	Water	Cl^-	0	Co^{2+}	13.0	0.1–1.0		25	216
AC	Water	Cl^-	0	Ni^{2+}	13.0	0.1–1.4		25	216
AC	Water	ClO_4^-	0	Zn^{2+}	20.0	0.1–0.7		25	216
S	Water–alcohol			Ag^+	2				222
S	Water–alcohol			Tl^+	4				222
S	Water–alcohol			Br^-	3				222
S	Water–alcohol			Cl^-	0				222
AF	Water			ArH_3N^+	3				223
AF	Water			$Ar_2H_2N^+$	2				223
CP	Sulfuric acid	HSO_4^-	0	Li^+	2.3				225
CP	Sulfuric acid	HSO_4^-	0	Na^+	3.0				225
CP	Sulfuric acid	HSO_4^-	0	K^+	2.1				225
CP	Sulfuric acid	HSO_4^-	0	NH_4^+	1.2				225
CP	Sulfuric acid	HSO_4^-	0	Ag^+	2.1				225
CP	Sulfuric acid	HSO_4^-	0	H_3O^+	1.8				225
CP	Sulfuric acid	HSO_4^-	0	Ba^{2+}	6.5				225
CP	Water	Cl^-	4	NH_4^+	2.2	1			228
CP	Water	Cl^-	4	NH_4^+	3	0.5			228
CP	Water	Cl^-	4	K^+	4.6	1			228
CP	Water	Cl^-	4	K^+	6.2	0.5			228
CP	Water	Cl^-	4	Ba^{2+}	22.1	0.5			230
CP	Water	Cl^-	4	Ba^{2+}	25.1	0.25			230
CP	Water	Cl^-	4	Ni^{2+}	24.5	0.5			231
CP	Water	Cl^-	4	Ni^{2+}	29.1	0.25			231
CP	Water	K^+	0	Li^+	10.3				232
CP	Water	K^+	0	Na^+	3				232
CP	Water	K^+	0	NH_4^+	0				232
CP	Water	K^+	0	H^+	9				232
CP	Water	K^+	0	Br^-	1				232
CP	Water	K^+	0	I^-	2				232
CP	Water	Cl^-	4	Li^+	11	1			233
CP	Water	Cl^-	4	Li^+	13.8	0.5			233
CP	Water	K^+	4.6	Br^-	3.5	1			234
CP	Water	K^+	6.2	Br^-	3.4	0.5			234
CP	Water	Cl^-	4	Ca^{2+}	23	0.5			235
CP	Water	Cl^-	4	Ca^{2+}	26.6	0.25			235
CP	Water	Cl^-	4	Sr^{2+}	22.7	0.5			236
CP	Water	Cl^-	4	Sr^{2+}	26.3	0.25			236
CP	Water	Cl^-	4	Mg^{2+}	24.1	0.5			237
CP	Water	Cl^-	4	Mg^{2+}	27.6	0.25			237
CP	Water	Br^-	3.5	Na^+	9.4	1			238
CP	Water	Br^-	3.5	Na^+	11.8	0.5 *M*			248
CP	Water	K^+	6.2	I^-	2.4	1 *M*			249
CP	Water	Cl^-	4	H^+	10.5	0.5 *M*			250
En	Water			H^+	5				251, 252
En	Water			H^+	5				253
En	Water			Li^+	5				190
En	Water			Na^+	4				190
En	Water			K^+	2				190
En	Water			Rb^+	2				190
En	Water			F^-	5				190
En	Water			Cl^-	2				190
En	Water			I	0.5				190

[a] E = equilibrium, IH = integral heats, AC = activity coefficient, S = solubility, AF = acidity functions, CP = colligative properties, En = entropy. [b] Except where noted.

Knowing the lower limit for K, the lower limit for n_{K^+} can be estimated. Equation 40 for NaCl and KCl is

$$K\left(\frac{n_{Na^+}}{2.36} - \frac{n_{K^+}}{2.71}\right) = 199 \qquad (52)$$

Here $r_{Na^+} + 1.38$ Å $= 2.36$, the quantity 2.71 was identified in eq 26, and $\beta_{NaCl} - \beta_{KCl} = 210 - 11 = 199$. Solving eq 66 for n_{K^+} gives

$$n_{K^+} = 2.71\left(\frac{n_{Na^+}}{2.36} - \frac{199}{K}\right) \qquad (53)$$

Since $n_{Na^+} > 3.05$ and $K > 976$, $n_{K^+} > 2.95$ from eq 53. From eq 39 the upper limit $n_{Li^+} = 4.23$ can be found.

A plot of the differential heat of solution, ΔH, for HCl *vs.* m gives a slope

$$\beta = \Delta H/\Delta m = 233 \text{ cal mol}^{-1}[m]^{-1} \qquad (54)$$

which can be used to narrow the limits of the n_{K^+} values and to estimate K.

The interactions of $H_{2+(\epsilon/e)}O^{(\epsilon/e)+}$ with each other and with chloride ions determine the difference in heat content of a mole of HCl in infinitely dilute and in m molal solutions. The ΔH *vs.* m plot indicated that an equation similar to eq 39 is satisfied. Thus

$$K\left(\frac{n_{H^+}}{R} - \frac{n_{Cl^-}}{3.19}\right) = 233 \qquad (55)$$

where $n_{H^+} = 4.6$ at 25° is the coordination number of water molecules in water; $R = 2.90$ Å from X-rays is the average distance of separation of neighboring molecules in water. n_{H^+} is also the coordination number of the $H_{2+(\epsilon/e)}O^{(\epsilon/e)+}$ ions not in the vicinity of chloride ions.

If eq 39 is subtracted from eq 55, there results

$$K\left(\frac{4.6}{2.90} - \frac{n_{K^+}}{2.71}\right) = 222 \qquad (56)$$

where $222 = \beta_{HCl} - \beta_{KCl} = 233 - 11$. But $K > 976$, and therefore from eq 56, $n_{K^+} > 3.68$. Let $n_{K^+} = {}^1/_2(3.68 + 4.02) = 3.8$. Substituting this value of n_{K^+} into eq 70 gives 1.17×10^3 for K. Using these values of n_{K^+} and K in eq 39 and 40, those for the coordination numbers, n, for various ions were obtained (see Table VII).

It can be seen that the coordination numbers of the monatomic ions in dilute aqueous solutions nearly equal the average coordination number (4.6) at 25° of the water molecule in water. The water structure it is thought[191,198,199] controls the structure on dilute aqueous solutions. The state of the ions in dilute solutions correspond to the envelopment of the ions by water molecules with the minimum change of water structure.[199]

From the integral heats of solution of CsI, NH_4Cl, and $NaClO_4$ in HCl and of $NaBr \cdot 2H_2O$ in HBr and $HClO_4$, the coordination numbers were calculated[200] for the ions (Table VII). The coordination nunber of ClO_4^- was that for which water molecules were perpendicular to the walls of the perchlorate tetrahedron. For the water molecules on the Cl–O line,[201] the coordination number was 7.3. Solvation numbers for Cs^+ and NH_4^+ ions were given (Table VI).

Table VII

Coordination Numbers, *n*, for Various Ions in Dilute Aqueous Solutions at 25°

Ion	*n*	*Ref*	*Ion*	*n*	*Ref*	*Ion*	*n*	*Ref*
Li^+	3.8	191	Cs^+	3.6	200	NO_3^-	6	211
Na^+	3.7	191	NH_4^+	4.2	200	Li^+	4	213
K^+	3.8	191	ClO_4^-	6.4	200	Na^+	6	213
Rb^+	3.8	191	Rb^+	3.8	203	K^+	8	213
Cs^+	3.8	191	Cs^+	3.5	203	Rb^+	8	213
Cl^-	4.4	191	K^+	3.8	204	Cs^+	8	213
Br^-	4.8	191	HSO_4^-	4.5	204	F^-	6	213
I^-	5.3	191	Li^+	3.4	205	Cl^-	8	213
Be^{2+}	3.3	191	Na^+	3.6	205	Br^-	8	213
Mg^{2+}	3.8	191	K^+	4.0	205	I^-	8	213
Ca^{2+}	4.0	191	NH_4^+	4.8	205	Na^+	4	214
Sr^{2+}	4.4	191	Rb^+	4.2	205	ClO_4^-	8	214
Ba^{2+}	4.8	191	Cs^+	4.2	205			
			Cl^-	4.7	205			
			Br^-	4.9	205			
			I^-	5.2	205			

Criteria for negative hydration of ions were derived.[202] It was concluded[203] from the thermochemical method that Rb^+ and Cs^+ ions were negatively hydrated. For their coordination numbers and those[204] for K^+ and HSO_4^-, see Table VII.

From the temperature dependence of the heats of solution of various electrolytes, the coordination numbers (Table VII) were found.[205] Integral heat of solution data[206] on UO_2^{2+} ion confirm Sutton's[207] view of $6H_2O$ molecules surrounding UO^{2+} ions in water. The changes with temperature of coordination numbers of Li^+, Na^+, K^+, Rb^+, Cs^+, and Cl^- ions were found[208] to be respectively −0, 44, 0.004, 0.10, 0.25, 0.49, and −0.074 per 10°. The heats of solution of K_2SO_4 in aqueous solutions of HCl were measured[209] at 25°. The coordination numbers of the ions identical with those listed in Table VII from ref 191 are given[210] along with Samoilov's solvation numbers listed in Table VI.

By thermochemical methods the coordination number and the structure (see Table II) of NO_3^- ion were determined,[211] and the effect of coordination number of thermochemical and thermodynamic properties of solutions was studied.[212]

Heats of hydration of salts have been selected[213] based on the heats of solution at infinite or very high dilution and of lattice energies. To find ionic heats, equal heats were assigned

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Cs^+ and I^- ions. In calculating the coordination numbers (Table VII) of the ions from their radii, the radius r_w of liquid water was used rather than 1.38 Å of a "frozen" hydrate envelope. The most probable coordination numbers of Na^+ and ClO_4^- ions in acetone were determined[214] (Table VII). The heat of proton solvation was studied.[215]

c. Activity Coefficient Methods

Applying volume statistics to an approximate Stokes and Robinson[216] model an equation for osmotic and activity coefficients was derived.[217] The "hydration numbers" obtained do not show the anomalies of the Stokes–Robinson hydration parameters. These workers, neglecting the covolume effect, obtained n^- values greater than any acceptable values for ionic hydration numbers, and which vary widely with the anion and in a direction opposite to that expected.[217]

Using volume fraction instead of mole fraction statistics, hydration and covolume effects can be combined into a single theory. Use of a mean hydration number h (or the Stokes–Robinson n) need not imply a sharp difference between "free" and "bound" water. For statistical purposes weak association of a large number of water molecules with an ion[218] is equivalent to strong adsorption of a small fixed number.[216] Using these assumptions and the Gibb's free energy for the solution of a hydrated electrolyte in volume fraction statistics, the equation for the mean electrolyte activity coefficient $\gamma_\pm$ was written

$$\log \gamma_\pm = \log {\gamma_\pm}^{\text{el}} + \frac{0.018mr(r + h - \nu)}{23\nu(1 + 0.018mr)} + \frac{h - \nu}{\nu} \log (1 + 0.018mr) - \frac{h}{\nu} \log (1 - 0.018mh) \qquad (57)$$

where h is the electrolyte hydration number, ν the number of ions per electrolyte molecule, $r = \phi_v/v^\circ_w$, ϕ_v the unhydrated electrolyte apparent molar volume, v°_w the mole volume of pure water, m the molality, and ${\gamma_\pm}^{\text{el}}$ the electrostatic contribution to the mean activity coefficient.

Equation 57 was used to calculate hydration numbers from data on activity coefficients.[219,220] In the calculations[216] the r was constant and applied to a concentration $m = 1$ for 1:1 and $m = 0.7$ for 2:1 electrolytes since at these concentrations eq 57 applies to all electrolytes. To find the hydration numbers (Table VI) of individual ions,[217] the halogen ions were assigned a hydration value of 0.9 and cesium was assigned that of zero.

Bernal and Fowler assumed the large anions were unhydrated. Stokes and Robinson[216] accepted that it is the cations rather than the anions that are hydrated. Their hydration number of cations (Table VI) are greater than those of Bernal and Fowler[155] from apparent molal volumes or of those of Glueckauf.[217] The increase in hydration number of a given cation with increasing anion size was discussed in relation to the binding of water molecules by the resultant field of an ion and its neighbors which depends on the dimensions of the ions. The anomalies of large hydration numbers of cations and of their increase with increasing anion size could be removed by adequate consideration of the volumes of hydrated ions.[221]

Solubility and activities of electrolytes were measured[222] in mixed solvents and hydration numbers (Table VI) of the electrolytes and ions and transsolvation constants calculated.

Seven arylmethanols were used[223] to establish the acidity function H_R in 44–64% H_2SO_4. The acidity function H_0 was obtained in 60–75% H_2SO_4 using amines. The data established the number of water molecules solvating the cations (Table VI).

d. Colligative Properties

Accurate freezing point depressions of solutions of metal hydrogen sulfates in sulfuric acid were measured[224] to determine the deviations from ideality of these solutions. Osmotic coefficients, ϕ, were calculated

$$\phi = \theta(1 + 0.002\theta)/6.12\textstyle\sum m_{ij} \qquad (58)$$

where θ is the molal freezing point depression measured from the freezing point of the standard state hypothetical undissociated sulfuric acid, and Σm_{ij} is the molality summed over the various ion types. Pure sulfuric acid has a minimum ionic strength, μ, of 0.0357 and a ϕ of 0.98. Its dielectric constant is 120 at the freezing point which does not necessarily mean that solutions in H_2SO_4 will be ideal.

The variation of the osmotic coefficient with molality is given by the equation

$$\phi = 1 + \phi_{\text{el}} + b\textstyle\sum m_{\text{i}} \qquad (59)$$

where ϕ_{el} is the electrostatic interionic contribution to the osmotic coefficient, Σm_{i} is the sum of the molalities of the ionic species, and b is a parameter related to the solvation numbers by

$$b = [(r + s)^2/40.8] - (r/20.4) \qquad (60)$$

where r is the ratio of the apparent molar volume of the electrolyte to that of the solute, 54 cm³. The Debye–Hückel theory is used to calculate ϕ_{el} using an appropriate distance of closest approach, a, for the dielectric constant $\epsilon = 120$. Both b and a are adjustable parameters. Equation 60 can be used to calculate solvation numbers (Table VI) for ions from freezing point data.[225]

Ionic substances in sulfuric acid solutions using proton magnetic resonance measurements were studied[225] and show that the solvation numbers are in the order $Na^+ > NH_4 \approx K^+ > Tl^+$.

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Much work[226–243] has been done on the ebullioscopic and cryoscopic determination of the total hydration of ions (Table VI) or of salts.

A method was devised[232] for obtaining solvation and association from colligative properties by graphical means and applied to the total solvation of $GaCl_3$ in CH_3Cl, proving the existence[233] of $CH_3ClGaCl_3$, and applied to the AlI_3–CH_3I and $AlBr_3$–C_6H_6 systems,[244, 245] confirming that a 1:1 complex existed in the AlI_3–CH_3I but not in the $AlBr_3$–C_6H_6 system.

e. Entropy of Hydration

Several authors[246–249] discussed entropy of hydration in conjunction with entropies of aqueous ions. The standard state chosen for the calculation of ionic entropies in aqueous solution is a 1 *m* solution of the ion obeying the perfect solution laws and the ions possessing the same partial molal heat content that they have an infinite dilution. These relative ionic entropies are referred to $S°_{298.1}$ of H^+ taken as zero.

The most direct method of obtaining ionic entropies in solution is to sum the ΔS of solution and the entropy of the solid salt. The ΔS of solution is calculated from the free energy, ΔG, and enthalpy, ΔH, of solution using the equation

$$\Delta G = \Delta H - T\Delta S \qquad (61)$$

The relative entropies referred to H^+ taken as zero, rather than these sums, are frequently given.

The so-called entropy of hydration is a function of the size and charge of the ion[246, 248]

$$\Delta S_{\text{hydration}} = f(e^2/r) \qquad (62)$$

where *e* is the charge and *r* the radius of the ion. The entropy of hydration is defined as the difference between the partial molal entropy of the ion in solution and its entropy in the gaseous state. This latter entropy, if translation can be calculated from the Sackur equation, is

$$S_{298.1} = \frac{3}{2}R \ln M + 26.03 \qquad (63)$$

where *R* is the gas constant in cal mol^{-1} deg^{-1}, *M* is the molecular weight, and 26.03 is the constant for the gas at 1 atm and 298.1 °K.

Linear plots of ionic entropies *vs.* the reciprocals of the ionic radii[250] indicated[248] that specific hydration effects are small compared to the electrostatic action of the charge on the water dipoles. Specific hydration effects do not exist, and chemical properties of solutions of ions are those of a given size, charged sphere in a medium of a certain dielectric constant, as was concluded earlier.[246] From ionic entropy[251, 252] the hydration numbers of the hydrogen ion and other ions[190, 253] were found (Table VI).

From the heats and free energies of several metal ions, the entropies of ammoniation were calculated and discussed[254] in relation to the hydration numbers. The idea[192] that when a water molecule binds to a cation the average entropy change approximately equals the heat of fusion of ice at 298° (6 kcal mol^{-1}), and the hydration number is obtained by dividing the absolute entropy of the gaseous ion by 6, was considered[254] an oversimplification because it does not consider the different strengths of binding of water molecules to a cation. Also the average contribution of 9.4 kcal mol^{-1} to the entropy of a hydrate per water molecule[255] is not adequate. Rather ion–dipole forces causing orientation and decrease of translational freedom of water molecules, and restriction from true covalent bonds between a donating center of solvent and the ion, must be considered. Which effect predominates when was considered. The results suggest that an ion carries no more water molecules covalently bound than ammonia. These results (Table VIII) were obtained assuming the entropy change for each molecule of water replaced by one of ammonia will equal the difference in the entropies of fusion of ammonia and of water at 298° (about −3 kcal mol^{-1}) and assuming the number of water molecules in the aquo cation is equal to the number of ammonia molecules in the ammine. If the ion carried more water than ammonia, the calculated entropy change would be more positive, whereas, except for the hydrogen ion, the measured results are more negative.[254] The larger decrease in entropy on ammoniation might partly be due to the shortening of the linkages in the ammines accompanied by correspondingly more configurational restrictions.

Table VIII

Ion	*No. of ligands*	$-\Delta S$ *calcd*	$-\Delta S$ *found*
H	1	3	−0.5
Ag	2	6	12.4
Cu	4	12	16
Ni	6	18	27
Zn	4	12	14
Cd	6	18	27
Hg	4 (2)	6 (12)	8
Li	3	9	12
Mg	4	18	19

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Different methods of calculating the values of heat, entropy, and energy of hydration of 15 lanthanides gave close agreement with experimental values.[256] Comments were made[257] on electrostatic volume and entropies of solvation. It was found that the compression of the ion has little effect on the free energy, entropy, or enthalpy of solvation, but thermal expansion of the cavity containing the ion affected the electrostatic entropy of solvation.

The entropy of exchange of negatively hydrated ions was studied.[258] The principal contribution of the entropy of exchange of the ions is the structural change entropy of water in the hydration of these ions.

f. Heat Capacity

From heat capacity measurements and calculations,[259] sodium ion was found more highly hydrated than potassium ion in aqueous solutions, and hydrogen ion was found to be H_3O^+.

From heat capacity data on LiOH and $LiOH \cdot H_2O$ and from the entropy change at 25° for the reaction $LiOH \cdot H_2O(cryst) \rightarrow LiOH(cryst) + H_2O(gas)$, it was confirmed[260] that the third law applied to the calorimetric entropies of both LiOH and $LiOH \cdot H_2O$.

Specific heats and hydration of ions were studied.[261,262] It was concluded that the hydrated ions contained 10 to 15 molecules of water in two energy layers, of which the second was dissociated at the higher temperatures used (140°).

The temperature dependence of the entropy, ΔS_h, energy E_h, and enthalpy of hydration, ΔH_h, for Li, Na, NH_4, and Mg halides and hydroxides were calculated[263] from heat capacity, $\bar{C}°$, and entropy, $S^{298}{}_{soln}$, data of ions in solution. Specific heats were measured[264] for solutions of $LaCl_3$, $NdCl_3$, $DyCl_3$, $ErCl_3$, and $YbCl_3$ at 25° from 0.1 *M* to saturation. From calculated apparent molal heat capacities and the concentration dependence of these or each solution, partial molal heat capacities of solute and solvent were obtained. From the data heavy rare earths have a lower coordination number than light rare earths. In nearly saturated solutions as in crystals,[265] ions of the type $[Cl_2Gd(OH_2)_6]^+$ were assumed to exist.

Specific heats indicated[266] that chlorides, bromides, and hydroxides of the alkali metals as well as HCl and HBr were hydrated.

g. Solubility and Dilution

From the difference in the heats of solution in dilute and concentrated solutions of KF and of $KF \cdot 2H_2O$ at 25° the heat of solvation of KF to $KF \cdot 2H_2O$ was found[267] to be 5912 cal mol^{-1}.

The solubilities of CO_2 in methyl and ethyl alcohol and in solutions of lithium and sodium chlorides, bromides, and iodides in these alcohols were determined[268] at 15 and 20°. In concentrated solutions these salts per mole combine with 3 to 5 mol of alcohol. In Table IX the solvations in infinitely dilute solution of three lithium halides and of sodium iodide obtained in methyl and ethyl alcohols, are compared with like solvation data from Ulich.[269] The two sets of measurements are in fair agreement. If the solvation of some reference ion were known, the solvation numbers of individual ions could be estimated.

Table IX

Solvation in Infinitely Dilute Solution of Lithium Halides and of Sodium Iodide in MeOH and EtOH[a]

	LiCl		*LiBr*		*LiI*		*NaI*	
Solvent	*U*	*L-E*	*U*	*L-E*	*U*	*L-E*	*U*	*L-E*
CH_3OH	11	8	9–11	8	7–10	9	5–9	8–9
C_2H_5OH	10–11	7	10	8–9	8–9	10	6–8	7

[a] U, Ulich; L-E, Lange and Eichler.

The solvation numbers, *S*, for the salts in the two alcohols were calculated as follows. The solubilities in moles of CO_2 per 100 mol of alcohol in the salt solutions and in the pure alcohols were, respectively, M''_{CO_2} and M'_{CO_2}. The moles of salt per 100 mol of alcohol is given as M_{salt}. Hence

$$S = 100\frac{1 - (M''_{CO_2}/M'_{CO_2})}{M_{salt}} = 100\frac{M'_{CO_2} - M''_{CO_2}}{M'_{CO_2}M_{salt}} \qquad (64)$$

If ΔM_{CO_2} is defined as

$$\Delta M_{CO_2} = 100\frac{M'_{CO_2} - M''_{CO_2}}{M'_{CO_2}} \qquad (65)$$

then

$$S = \Delta M_{CO_2}/M_{salt} \qquad (66)$$

The solubilities of some strong electrolytes in alcohols were calculated[270] from their solubilities in water from a formula involving only the charges and radii of the ions and the dielectric constant of the solvent. The K^+, Rb^+, Cs^+, Cl^-, Br^-, and ClO_4^- ions were found to occupy the same volumes in solution as in the crystalline salts. Hence there was no enrichment of either the water or alcohol around the ions, and these ions were not solvated. From the abnormal solubility curve of NaCl the Na^+ ion was hydrated.

The temperature coefficients of the solubilities of salts were studied.[271,272] The temperature coefficient of solubility

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for similar salts increased with the degree of hydration of the "dominant ion."

The solubility of isoamyl alcohol in aqueous alcohol mixtures in the absence and in the presence of the sodium and potassium halides was discussed,[273] and the results were attributed to hydration of the ions and their action on the alcohols. The action decreased in the order $Cl^- > Br^- > I^-$, while the cations caused an inversion of the lyotropic series.

The solubilities of KNO_3 as affected by the presence of KNCS and KBr in aqueous solutions were presented[274] in the light of the effects of these salts on the NCS^- and Br^- ions. The two systems were chosen because KNCS and KBr differ in ion structure but have the same hydration energy, 72 kcal/g-ion.[212]

The solubility of silver bromate in sucrose–water and in tetrahydrofuran–water was studied.[275,276] The solvation radius of $AgBrO_3$ was calculated to be about 1 Å from 20 to 30°.

The influence of the interaction of large univalent ions with water structure was investigated using solubility.[277] If the order of the orderliness in the tetrahedral water cell was reduced by the intercalation of the ions in the cell, the effect of the nonhydrating univalent ions was characterized as their "negative hydration." [278] The negative hydration decreased in the order $NO_3^- < Br^- < SCN^-$.

From studies of the solubility of silver bromate in water–glycerol solvents, the solvation radius of the $AgBrO_3$ was calculated[279] to be 3–4 Å. From similar data in water–propyl alcohol solvents, the solvation radius of lead sulfate was found[280] to be 1–6 Å.

Solubilities of $AgBrO_3$ in water–urea and water–methanol solvents were investigated.[281,282] The solvation radii for $AgBrO_3$ were 5.5–7.6 Å in the former solvent and 0.5–1.3 Å in the latter solvent.

The influence of the character of the solvent and of the solvation of uranyl nitrate on its solubility in water–bis(2-chloroethyl) ether and in water–diethyl ether at 25° was studied.[283]

The polytherm of the $NaI\text{–}KBr\text{–}H_2O$ system was investigated. The hydrates $NaBr \cdot 2H_2O$, $NaBr \cdot 5H_2O$, $NaI \cdot 2H_2O$, and $NaI \cdot 5H_2O$ were observed.[284,285]

The solubility of rubidium and cesium nitrates in H_2O_2–H_2O solvents were measured[286] at 0, 15, and 25°. In solid phases in the $RbNO_3\text{–}H_2O\text{–}H_2O_2$ system the solvates $RbNO_3 \cdot {}^3/_7H_2O_2$ and $RbNO_3 \cdot {}^1/_2H_2O_2$ were found. The formation of hydroxyperoxidates by KNO_3 and $RbNO_3$ indicates these ions may be more highly solvated in H_2O_2 solutions than in H_2O. The solubilities of the alkali nitrates in 100% H_2O_2 increased as the diameter of the cation increased up to cesium when the smaller field strength of the ion counteracts the tendency of H_2O_2 to solvate the larger ion and thus decreases the solubility.

Double salts and complexes in saturated solutions of inorganic salts[287–292] were studied. Total hydration numbers[293] were used to describe solubility isotherms of ternary systems with water as a component. True total hydration numbers in saturated aqueous solutions of two inorganic salts are constantly independent of the analytical composition of the solution.[291]

The effects of salts on the solubility of benzoic acid in 50% aqueous solutions of EtOH, MeOH, Me_2CHOH, and dioxane mixed solvents were determined.[294] The different salting-out effects are attributed to the solubility of some compounds in organic solvents, the molecules of which are used for solvation. Lithium salts depressed the solubility of naphthalene in 50% MeOH much more than did sodium compounds.[295] Lithium salts are soluble in alcohol, and are both hydrated and solvated with methanol molecules and thus do not increase the relative concentration of alcohol in the solution. The papers on solubility discussed above give solvation of salts rather than solvation of ions and discuss solvation by nonaqueous solvent components.

h. Structure and Ionic Heats and Entropies

From the structure of divalent ionic solutions, the ionic heats of hydration of these ions in aqueous solutions at 25° were found[296] to depend on four terms, the cationium sheath being the major contribution. The most probable permanent solvation number was determined to be 4 for the metals of group IIa, 6 for metals of group IIb, and 4 and 6 for transition divalent ions. The nature of the permanent-type linkage is given. The conflict of opinion on the nature of solvation bonding was discussed.[297]

Heats of hydration and hydration numbers for the hydrogen and hydroxide ions at 25° were examined.[298] Concentration variation of solvation is qualitatively predicted. The formula of H^+ and OH^- ions in water, in the ideal case, could be given as $(H_3O^+) \cdot (H_2O)_3(H_2O)_9$ and $(OH^-) \cdot (H_2O)_{4.7}(H_2O)_{17}$. The arrangements of the H_2O molecules around the H_3O^+ and OH^- ions were given. Table X contains[299] variousy hydration numbers for hydrogen and Table XI those for hydroxide ions found by different methods.

Positive and negative hydration of ions (Table XII) has been discussed with respect to structural changes in water

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Table X

Values of the Hydration Number for the Hydrogen Ion in Aqueous Solution at Room Temperature by Various Investigators Using Various Methods[144]

Year	*Author and methods*	*Hydration no.*	*Ref*
1930	Ulich (entropy)	4	251
1954	Azzam (theoretical)	3.9	298
1954	Wicke, *et al.* (heat capacity)	4	304
1955	Glueckauf (activity coefficient)	4	217
1955	Glueckauf (uptake by ion exchange)	4	218
1957	Bascombe, *et al.* (activity function)	4	300
1957	Ackermann (heat capacity, infrared)	4	301
1957	Van Eck, *et al.* (X-ray, solution)	4	302
1957	Eigen	4	303
1957	Falk, *et al.*	4	304
1958	Beckey	4	305
1920	Bjerrum (activity)	9	306
1936	Bourion, *et al.* (cryoscopic)	10	307
1947	Van Ruyen (vapor pressure)	13	308
1948	Hasted, *et al.* (dielectric)	10	309
1941	Darmois (density)	0.3	310
1909	Washburn (Hittorf transference) (1 *N*)	1	311
1927	Remy (parchment paper) (1 *N*)	1	312
1938	Baborovsky (1 *N*)	1	313
1938	Baborovsky (0.1 *N*)	5	313

Table XI

Hydration Numbers of Hydroxide Ions

Year	*Authors and methods*	*Solvation no.*	*Ref*
1920	Bjerrum (activity)	7.6	306
1941	Darmois (density)	0	310
1947	Van Ruyen (vapor pressure)	8	308
1955	Glueckauf (activity)	4	217, 218
1957	Van Eck (X-ray, solution)	4	302
1957	Ackermann (heat capacity)	6	301
1957	Ackermann (infrared)	3	301
1960	Azzam (theoretical)	4.7	298

and with respect to positive and negative entropies of hydration.[314–316]

Table XII

Ions Showing Positive and Negative Hydration

Type of hydration	
Positive	OH^-, $HCOO^-$, HF_2^-, HCO_3^-, BrO_3^-, HS^-, CO_3^{2-}, SO_3^{2-}, SO_4^{2-}, CrO_4^{2-}, SeO_4^{2-}, MoO_4^{2-}, SiF_6^{2-}, PO_4^{3-}, AsO_4^{3-}
Negative	NH_4^+, OCN^-, CN^-, NO_3^-, ClO_3^-, HSO_4^-, HSe^-, ReO_4^-, ClO_4^-, MnO_4^-, IO_4^-

i. Polarography

Polarographic data on some complex ions of Cu, Zn, Cd, and Pb were used to calculate[317] the approximate molecular weights of the ions using the Riecke formula;[318] from these were obtained the degree of hydration of Cu, Zn, and Cd ions; Pb did not hydrate.

From half-wave potential, $E_{1/2}$, of Cd^{2+} and Ti^+ ions in sulfuric acid, it was concluded[319] that in 17 *F* sulfuric acid Tl^+ binds 2.3 times as many water molecules as does Cd^{2+} ions.

Polarography was used[320] to study the hydration of certain bivalent ions in MeOH–H_2O solvents. Each ion showed a regular decrease in $E_{1/2}$ with increasing water concentration. Table XIII contains the values for the ions of the stability constants in NH_4ClO_4 solutions for steps of the type $M^{2+}A_n(H_2O)_m + H_2O \rightarrow M^{2+}A_{n-1}(H_2O)_{m+1} + A$. Tl^+ was not hydrated in these solutions. From polarographically determined formation constants of the oxalate complexes of Cu(II) and Cd(II) in light and heavy water it was concluded[321] that light water is more strongly solvating than is heavy water.

Table XIII

Stability Constants for Various Bivalent Ions in NH_4ClO_4 Solutions

NH_4ClO_4, M	*Ion*	*K_1*	*K_2*	*K_3*
0.01	Cd^{2+}	0.36	2.00	2.7
0.05	Cd^{2+}	0.59	2.00	3.6
0.1	Cd^{2+}	0.60	1.65	
0.05	Pb^{2+}	0.83	2.10	
0.10	Pb^{2+}	0.46		
0.01	Zn^{2+}	0.50	1.67	2.30

The solvations of bivalent metal ions in organic component–water and in mixed organic solvent systems were investigated.[322,323] In the case of acetone–methanol, acetone–ethanol, and acetone–water systems, the general type of complexes were shown to be $[M(ROH)_i(Me_2CO)_{n-1}]^{2+}$ where *n* is the coordination number, M = Cd or Pb, and R = H, Me, or Et. Cd formed six hydrates and four solvates

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in MeOH and none in EtOH. Pb formed five hydrates, and two solvates with MeOH and three with EtOH. In acetone–alcohol solvents the method of DeFord and Hume[324] was used in calculating the composition and formation constants of the complexes.

For solvation numbers of Cd^{2+}, Pb^{2+}, and Zn^{2+} ions in mixed solvents, see Table XIV. For Cd^{2+} the coordination numbers in MeOH were 1 and 2 and for EtOH 1, 2, and 3.

Table XIV

Solvation Numbers for Cd^{2+}, Pb^{2+}, and Zn^{2+} in Formamide–Methanol, Formamide–Ethanol, and Formamide–Water Solvents

Ion		*Methanol*	*Ethanol*	*Formamide*	*Water*
Zn^{2+}	$CHONH_2$–MeOH	2		2	
Pb^{2+}	$CHONH_2$–MeOH	2		2	
Zn^{2+}	$CHONH_2$–EtOH		4	2	
Pb^{2+}	$CHONH_2$–EtOH		4	2	
Zn^{2+}	$CHONH_2$–H_2O			0	0
Pb^{2+}	CH_2ONH_2–H_2O			0	0
Cd^{2+}	CH_2ONH_2–H_2O			0	0

j. Addenda to Thermodynamic Studies

Some general thermodynamic studies of ion hydration have been made. Noyes found[325,326] that the singly charged d^{10} ions, Cu^+, Ag^+, and Au^+, showed extreme solvation effects observed for no other ions, including the isoelectronic species Zn^{2+}, Cd^{2+}, and Hg^{2+}. He found that the thermodynamic properties change more for the hydration of anions than for cations of the same size, and that the available data do not exhibit the monotonic variation with ionic size as do cations.

The simple electrostatic model, ion–solvent interaction, and bivalent sulfates in water have been discussed.[327] To understand the associational behavior of KI in a variety of solvents and of the bi-bivalent sulfates in water, one must account for the molecular nature of the solvent. It was concluded[328] that something radically different from the primitive theories is needed for the interpretation of ionization and solvation phenomena.

Enthalpies of solution of calcium, strontium, and barium chlorates and bromates in amides were reported.[329] Solvation energies were evaluated and compared with those using a Born model. If hydrogen bonding in the solvent is preferential to the formation of ion–solvent interactions, then the least "structured" solvents will have the greatest ion-solvating influence.

Experimental and absolute ionic enthalpies were evaluated[330] for the alkali and halide ions in formamide. The absolute enthalpies of solvation were interpreted in terms of the interaction of the ion with six-coordinated formamide molecules. The polarization energy of the solvent beyond the first shell was taken into account.

The real free energies of solvation of ions were measured in nonaqueous and mixed solvents.[331] The experimental real free energy of species i in solvent s, α_i^s, is the free energy change in the process when an ion in field free space is inserted into a large quantity of solution s with no net electrical charge. For the Debye–Hückel region of activity a_i

$$\alpha_i^s = \alpha_i^{s,\phi} + RT \ln a_i \qquad (67)$$

where $\alpha_i^{s,\phi}$ is the standard real free energy obtained by extrapolation. The standard real free energy was divided into bulk and surface contributions. The former is identified with the "chemical" solvation energy which is the quantity desired in separating the free energy of solvation of a salt into its ionic components.

A discussion was presented[332] on ionic solvation in mixed aqueous solvents and the changes in free energy accompanying transfer of electrolytes from water to mixed aqueous solvents.

The thermodynamic treatment of a mixed fluid in electrostatic field is applied[333] to preferential solvation interpreted on the basis of partial molal free energies, at infinite dilution in mixed solvents.

A method was proposed[334] for calculating the individual and average activity coefficients of ions in solution based on the simultaneous consideration of the electrostatic interaction of the ions and of their solvation. A change in the enthalpy of solvation with change in concentration causes the change in the activity coefficients.

The solvation of hydrogen ion by water molecules in the gas phase was investigated.[335] Equilibrium constants and the thermodynamic functions for the reactions $H^+(H_2O)_{n-1} + H_2O \rightarrow H^+(H_2O)_n$ were determined. The structures of the hydrates $H^+(H_2O)_n$ change quite continuously and no single structure showed dominant stability. In the lower hydrates (n = 2–4 or even 6) all water molecules appear to be equivalent. Thus the notation $H_3O^+(H_2O)_n$ is inappropriate. Beyond $n = 4$, a new shell is started or crowding of the first "shell" occurs. The solvation of the sodium ion is also discussed.

Thermodynamic functions of solvation of ions have been calculated theoretically.[336] The conditions for positive and for negative hydration of ions have been discussed theoretically.[337]

Negative hydration of ions has been found[338] to occur in the interval from the freezing point up to some limiting temperature. The temperature effect on near hydration is greater than on far hydration since most of the entropy characteristics in the variation of the structure of water are close-up effects. Near hydration may be negative as well as positive.

Solvent activity coefficients corroborate the qualitative observation that small densely charged anions are more strongly solvated by protic solvents than by dipolar aprotic

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solvents.[339] For large polarizable anions the opposite is true. Very large and polarizable anions are more solvated by methanol than by water. Cations are more solvated by DMF, DMSO, and HMPT than by water.

The statistical thermodynamics of solvation has been used[400] to derive an equation relating the change in volume in solution, the free energy of solvation, and the isothermal compressibility of the solvent.

Solvates of alkali metal methylates with methanol were determined[401] by thermal analysis. Coordination numbers of 4, 6, 6, 8, and 8 for Li^+, Na^+, K^+, Rb^+, and Cs^+, respectively, were found.

Variation of the entropies of hydration of the lanthanide series support a change in the hydration number of the lanthanide ions somewhere in the middle of the series, from Nd to Tb.[402] Variation in thermodynamic properties observed in complexation reactions often result from dehydration of the ions rather than of the ligation. Values of the hydration numbers of La and Lu ions were calculated[403] as 7.5 and 8.7, respectively. The ratio is 1.2 which is that found[402] for the entropies of hydration of Lu and La ions. This might imply that the hydration sphere is 20% greater in the heavier lanthanides.

E. DIFFUSION

1. Theory

Diffusion coefficients are generally calculated[404–406] using the Onsager–Fuoss equation, which for calculating the diffusion coefficient, D_{calcd}, of a binary electrolyte is

$$D_{\text{calcd}} = 2000RT\,\frac{\overline{M}}{C}\left(1 + C\,\frac{\partial \ln y_{\pm}}{\partial C}\right) \tag{68}$$

where R is the molar gas constant in ergs $\text{deg}^{-1}\ \text{mol}^{-1}$, T is the absolute temperature, $\overline{M}$ is a function in diffusion theory, C is the molar concentration of the solution, and $y_{\pm}$ is the mean activity coefficient of an electrolyte.

From the calculated and observed values of the diffusion coefficient, the solvation number, n, of the electrolyte can be found from

$$D_{\text{obsd}} = D_{\text{calcd}}(1 - 0.018n) \tag{69}$$

2. Experimental Technique

Diffusion coefficients can be obtained from conductivity measurements as a function of time.[407,408] If K_B and K_T are the reciprocal resistances measured at the bottom and top of the cell, then

$$\ln (K_B - K_T) = \frac{t}{\tau} + \text{constant} \tag{70}$$

where t is the time and τ is defined by the equation

$$1/\tau = \pi^2 D/a^2 \tag{71}$$

in which a is the height of the cell. Also $1/\tau$ is the slope of the line obtained when $\ln (K_B - K_T)$ is plotted *vs.* t. From the slope of the line, D can be calculated from the equation

$$D = \frac{a^2}{\pi^2}\frac{1}{\tau} \tag{72}$$

This is the D_{obsd} of eq 69.

There are other methods for obtaining diffusion coefficients such as the porous diaphragm approach.[409,410]

3. Solvation Numbers Determined

From the measurement of the diffusion coefficient in calcium chloride in aqueous solution and using eq 69, the hydration number of $CaCl_4$ was found to be approximately 24 which does not agree with the value of 11.9 found[411] from activity studies.

From diffusion coefficient measurements, degrees of hydration of metallic ions were obtained (Table XV) which agreed with those obtained by reliable methods.[412]

It was found[413] from diffusion and mobility studies that, for complex ions containing one metallic atom, the number of water molecules, m, in the inner coordination sphere of an ion was given by

$$m = (n - 1)/3 \tag{73}$$

where n is the number of atoms composing the ion.

The hydration of ions as determined[414] using parchment membranes are listed in Table XV. With increasing dilution the hydration number of anions tends toward a common limiting value, indicating a physical nature for hydration in dilute solutions and a chemical nature in concentrated solutions. From diffusion measurements using a membraneless cell,[415] copper and nickel ions have the numbers of waters per ion given in Table XV.

Of dialysis and diffusion methods, only diffusion measurements give a reliable degree of hydration.[416] Choosing a reference ion, for each valence group (Tl^+, Ba^{2+}, Bi^{3+}, Th^{4+}), the degrees of hydration of other ions are given in Table XV. Ulich's[417] value of 2 for Tl^+ yields other hydration values for the other ions.

In methods of diffusion the reference substance, for example, allyl alcohol, is carried by the electrolyte.[418] In some instances the electrolyte was found to carry more reference

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Table XV

Solvation Numbers of Ions from Diffusion Measurements

Solvent	*Temp, °C*	*Ref ion*	*Solvn no. of ref ion*	*Ion*	*Solvn no. of ion*	*Ref*
Water	25			Li^+	5	412
Water	25			Na^+	3	412
Water	25			K^+	1	412
Water	25			Rb^+	1	412
Water	25			Cs^+	1	412
Water	25			Tl^+	1	412
Water	25			Ag^+	2	412
Water	25			Cl^-	1	412
Water	25			Br^-	1	412
Water	25			I^-	1	412
Water	25			Mg^{2+}	9	412
Water	25			Ca^{2+}	9	412
Water	25			Sr^{2+}	9	412
Water	25			Ba^{2+}	8	412
Water	25			Cu^{2+}	11	412
Water	25			Zn^{2+}	11	412
Water	25			Cd^{2+}	11	412
Water	25			Co^{2+}	13	412
Water	25			Fe^{2+}	12	412
Water	25			Mn^{2+}	12	412
Water				Li^+	62	414
Water				Na^+	44.5	414
Water				K^+	29.3	414
Water				H^+	5	414
Water				Cl^-	26.6	414
Water				Br^-	29.6	414
Water				I^-	21.4	414
Water				Cu^{2+}	7–8	415
Water				Ni^{2+}	10	415
Water	10	Tl^+	0	K^+	9.5	415
Water	10	Tl^+	0	Cl^-	3.5	416
Water	10	Tl^+	0	I^-	10	416
Water	10	Ba^{2+}	0	Be^{2+}	10	416
Water	10	Ba^{2+}	0	Mg^{2+}	9	416
Water	10	Ba^{2+}	0	Zn^{2+}	9	416
Water	10	Ba^{2+}	0	Cu^{2+}	7.4	416
Water	10	Ba^{2+}	0	Ni^{2+}	8.5	416
Water	10	Bi^{3+}	0	Al^{3+}	13	416
Water	10	Bi^{3+}	0	Y^{3+}	11	416
Water	10	Bi^{3+}	0	Ce^{3+}	6.7	416
Water	10	Bi^{3+}	0	Cr^{3+}	16.5	416
Water	10	Bi^{3+}	0	Fe^{3+}	10.5	416
Water (H_2O or D_2O)				Li^+	22	423
Water (H_2O or D_2O)				Na^+	13	426
Water (H_2O or D_2O)				K^+	7	426
Water (H_2O or D_2O)				Cs^+	6	426
Water (H_2O or D_2O)				Cl^-	5	426
Water (H_2O or D_2O)				Br^-	5	426
Water (H_2O or D_2O)				F^-	7	426
Water (H_2O or D_2O)				NO_3^-	6	426
Water (H_2O or D_2O)				CH_3COO^-	11	426

substance than water.[419] Pyridine as a reference substance was observed to combine in large proportions with silver ion in the electrolysis of silver nitrate solution.[420]

The theoretical treatments of diffusion, self-diffusion of electrolytes, and hydration effects were discussed.[421] The addition effect of counterdiffusion of the solvent was pointed out. A potential barrier was assumed over which ions in water jump either alone or together with their hydration shells.[422] Using the mobility and the coefficient of self-diffusion of the ion and the absolute temperature, the change in the potential barrier was found to be positive for Li^+, Na^+, Mg^{2+}, and Ca^{2+} and negative for K^+, Cs^+, Cl^-, Br^-, and I^-. For these latter ions, water molecules remain in their vicinity a shorter time than in the vicinity of other molecules. The activation energy for the solvent between solvent bound by the ion and free solvent was the main quantity characteristic of the solvation of ions.[423] When this was negative the water near the ions became more mobile than in pure water. This was called negative hydration.

Experimental diffusion coefficients in solutions of $LiNO_3$ and LiCl agreed with the theoretical values using the equation deduced assuming that only molecules of water attached directly to Li^+ moved with the ion.[424]

From nuclear magnetic resonance spin-echo techniques, hydration numbers, Z, were deduced using self-diffusion coefficients, D, and concentrations, C, and assuming rapid exchange between "free" and "hydrated" water.[425] Thus

$$\frac{D_{\text{solution}}}{D_{\text{pure water}}} = 1 - Z\frac{C_{\text{ion}}}{C_{\text{water}}} \tag{74}$$

In LiCl, $Z = 4$, with Li^+ the hydrated species since $Z < 1$ in HCl; in $Th(ClO_4)_4$, $z = 30$; and in $Be(ClO_4)_2$, $Z = 6$ for low and $Z \cong 16$ for higher concentrations.

A potential applied across a membrane separating a 0.3 N electrolyte solution in H_2O from a 0.3 N electrolyte solution in D_2O caused a current to flow accompanied by the passage of H_2O or D_2O through the membrane, depending on the direction of flow of the current.[426] The H_2O and D_2O relative solvation numbers were calculated. Absolute solvation numbers were obtained from the relative ones by conductivity measurements (Table XV).

The coefficient of self-diffusion for water in aqueous 0.5 M solutions of KCl, NaCl, and KI were measured using a nuclear magnetic spin-echo relaxometer at 21–23°.[427] The hydration of Na^+ was found to be positive and those of K^+, I^-, and Cl^- were negative.

Using radioisotopes as tracers, measurement at 25° of self-diffusion coefficients of ions and solvents from 0.1 M to saturated solutions of LiCl, NaCl, KCl, and $CaCl_2$ were made.[428] The hydration of Cl^- was found to be weak and constant, suggesting a hydrogen bond with water. The hy-

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dration number of cations diminished with increased concentration.

The negative hydration of ClO_4^- and NH_4^+ ions was observed by determining the self-diffusion and the macroscopic viscosity in aqueous solutions of perchlorate and ammonium salts.[429]

4. Significance

The method of diffusion depending on conditions can yield widely divergent results. Thus lithium ion may have a solvation number of 5, 22, or 62. The value of 62 from a parchment paper diaphragm measures the primary, and also secondary, solvation sheaths of the ion. The value of 22, from imposing a high potential across the diffusion cell, involves at least two or three solvation shells of the lithium ion. The hydration number is limited to the primary solvation shell.

There is not a consistent order of solvation of the ions within a family, though the order in the alkai metal ions is ordinarily $Li^+ > Na^+ > K^+$. The halogen family of ions tends to show the order of hydration $I^- > Br^- > Cl^-$, though in some cases $I^- = Br^- = Cl^-$, $K^+ = Rb^+ = Cs^+$, and $Mg^{2+} = Sr^{2+} = Ca^{2+} \cong Ba^+$. The orders of solvation in some cases, *e.g.*, halogen ions, are opposite to those by other methods.

In the author's opinion diffusion is one of the less dependable and less consistent methods of measuring solvation, and the method gives data most difficult to rationalize and interpret.

F. ISOTOPIC EQUILIBRIUM

1. Theory

Ionic hydrates $A(H_2O)_n^z$ are considered to exist only if characteristic internal vibrations can be detected by spectral or other effects.[430] The investigation proposed to show the connection between the fractionation by ions[431] of the oxygen isotopes in solvent water and ionic hydration.

The ionic hydrates will cause group vibrations of bound isotopic water molecules differing in their zero-point vibrational energy levels owing to difference in their masses. Such difference decreased the activity of the heavier relative to the ligher species as indicated by the equation

$$\alpha \times 10^3 \equiv 1 - \frac{R}{R_0} = \sum\nolimits_A m_A n_A (K_A - 1)/55.51 \qquad (75)$$

where α is the enrichment factor, R the ratio of the activity of the heavy to light species in the solution, R_0 the ratio of the activity of the heavy to light species in solvent only, m_A the molality of ion A, N_A the hydration number of ion A, K_A the intensity factor K_1/n_0, and K_1 the equilibrium constant for the reaction

$$A(H_2O)_n + H_2O^* \rightleftarrows A(H_2O)_{n-1}(H_2O^*) + H_2O \qquad (76)$$

where the asterisk indicates the heavier species.

The following assumptions in deriving eq 75 were made: (a) heavy and light water formed an ideal solution; (b) solute did not change the gross isotopic composition of water; (c) in the water replacement reactions, successive steps differed only by a statistical factor, *i.e.*

$$A(H_2O)_n + H_2O^* \rightleftarrows A(H_2O)_{n-1}(H_2O)^* + H_2O \qquad (77)$$

$$K_1 = n_A K_A$$

$$A(H_2O)_{n-1}(H_2O^*) + H_2O^* \rightleftarrows A(H_2O)_{n-2}(H_2O^*)_2 + H_2O \qquad (78)$$

$$K_2 = (n_A - 1)K_A/2, \text{ etc.}$$

2. Experimental

One method of determining the enrichment and intensity factors, and thus the hydration number of ion A, n_A, was to dry solutes to the anhydrous states and dissolve with minimum exposure to air in distilled water stored in Pyrex vessels. The solutions were degassed by repeated cycles of freezing, pumping, and thawing, and carbon dioxide was admitted to the equilibration vessel. After equilibration from 5 to 30 days at a controlled temperature, the gas was sampled, dried, and measured for isotopic ratio using a mass spectrometer. The isotopic ratio (mass 46/mass 44) is a measurement which reflects the relative activity of the water species *via* the equilibrium

$$H_2{}^{18}O(soln) + C^{16}O_2(gas) \rightleftarrows H_2{}^{16}O(soln) + C^{18}O_2(gas) \qquad (79)$$

Pure water, treated, measured, and sampled as above, was the standard used for comparison. The standard deviation of a single measurement of α was ± 0.02.

3. Solvation Numbers Determined

In the determination of the enrichment factor, it was found[430] that a reasonable and consistent distribution of the separate effects due to cation and anion could be made only if in the detection of characteristic internal vibrations, the ions ClO_4^-, Cl^-, I^-, Na^+, and $Co(en)_3{}^{3+}$ were not hydrated. Table I contains the hydration numbers.

The results of equilibrium data of HCl solutions containing radioactive alkali metal chlorides and of LiCl and KCl solutions containing radioactive Na with synthetic ion-exchange resins were discussed in terms of the Harned rule and the hydration theory of Stokes and Robinson.[432] Competitive hydration of cations was indicated in mixed electrolyte solutions.

In the exchange of chromium between Cr(II) and Cr(III) using radioactive techniques, the effect of ion hydration and of chloride complexing on the rate of exchange is discussed.[433] Such ions as $CrCl_2(H_2O)_4{}^+$ and $Cr(H_2O)_6{}^{3+}$ are mentioned.

The use of oxygen isotope in the study of the hydration of ions was discussed.[434] An equilibrium method which involves the study of the measurement of the effect that salts exert on the activity ratio of $H_2{}^{18}O$ compared to $H_2{}^{16}O$ in the liquid was suggested.

Isotopic exchange equilibrium data of the $H_2{}^{18}O$ and $H_2{}^{16}O$ concentrations in the body of the liquid (K_1) and in the vicinity of the ions (K_h) and of the energy involved (ΔE) were used to formulate the criteria for negative hydration of ions.[435] These criteria were $K = (K_1/K_h) < 1$ and $\Delta E < 0$.

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Table XVI

Solvation Numbers of Ions Determined by the Isotopic Equilibrium Method

Solvent	*Temp, °C*	*Ref ion*	*Solvn no. of ref ion*	*Ion*	*Solvn no. of ion*	*Ref*
Water	25	ClO_4^-, etc.	0	Li^+	1.0	430
Water	4	ClO_4^-, etc.	0	Li^+	2.0	430
Water	25	ClO_4^-, etc.	0	Ag^+	0.7	430
Water	4	ClO_4^-, etc.	0	Ag^+	0.7	430
Water	25	ClO_4^-, etc.	0	H^+	4.6	430
Water	4	ClO_4^-, etc.	0	H^+	2.0	430
Water	25	ClO_4^-, etc.	0	Mg^{2+}	6.2	430
Water	4	ClO_4^-, etc.	0	Mg^{2+}	7.1	430
Water	25	ClO_4^-, etc.	0	Cr^{3+}	19 ± 10	430
Water	25	Cr^{3+}	6.0	Al^{3+}	6.0 ± 0.5	436

A method for rapid mixing and sampling in the isotope dilution technique of studying ionic hydration gave the data in Table XVI.[436]

In a kinetic study of the isotopic exchange between $[Lu(EDTA)(H_2O)]^-$ and Lu^{3+}, a simple displacement reaction was suggested for the exchange.[437]

Solvent isotope effects and ionic hydration equilibrium for H_2O-D_2O mixtures can be calculated from the structure differences between D_2O and H_2O and that between HDO and H_2O and the relative amounts of H_2O, D_2O, and HDO.[438]

The flow method of isotope dilution was used[439] to study hydration, polymerization, oxidation, and reduction of aquo cations.

In the study of the exchange of water between oxygen-18-labeled solvent and aquorhodium(III) ion using the isotopic dilution procedure, the hydrated ions $Rh(H_2O)_6^{3+}$, $Rh(H_2O)_5OH^{2+}$, $Rh(H_2O)_5^{3+}$, and $Rh(H_2O)_4OH^{2+}$ were used to explain the exchange rate.[440]

The solvation of Cr(III) ion in acidic water–methanol solvents was investigated using ion-exchange and isotopic dilution procedures.[441] At 60° the composition of the Cr(III) ion varied from $Cr(H_2O)_{5.831}(MeOH)_{0.169}^{3+}$ to $Cr(H_2O)_{2.40}(MeOH)_{3.60}^{3+}$ when the H_2O-MeOH solvent ranged in composition from 0.154 to 0.982 mol fraction of MeOH, respectively. With respect to first shell coordination, Cr(III) ion discriminates in favor of H_2O over MeOH.

In water–ethanol mixed solvents, separation by ion-exchange methods of individual differently solvated species, $Cr(OH_2)_{6-n}(OHC_2H_5)_n^{3+}$ (n = 0, 1, 2, and 3), present in equilibrated solutions were made.[442] The average number of ethanol molecules, $\bar{n}$, per Cr(III), is the same at 50 and 75°, and thus the enthalpy change for the solvent replacement reaction is small (0 ± 0.5 kcal/mol).

4. Significance

No general trend of hydration number with temperature is evident, though cations other than hydrogen apparently have the same or greater hydration numbers at lower than at higher temperatures. Ions perhaps would be more highly solvated at lower than at higher temperatures, since at lower temperatures decreased thermal agitation would permit stronger attraction between ions and solvent molecules. That hydrogen ion is less solvated at lower temperature might be due to stronger hydrogen bonding among water molecules at lower temperature which prevents breaking down of water structure by protons and the consequent formation of hydronium and other hydrated hydrogen ions. The hydration number exhibits a variation with ionic charge, radius, and type which is qualitatively reasonable.[443]

Some ions found unhydrated by this approach, namely ClO_4^-, Cl^-, I^-, and Na^+, evidence hydration by other methods. The cation with a completed inner sphere, $Co(en)_3^{3+}$, shows zero hydration probably because of the identity of the hydration number and the number of water molecules in the inner sphere.

As do several other methods, this procedure shows, in general, increasing hydration with increasing ionic valence. The lithium ion by this method has a relatively low hydration number, in contrast with nmr procedures which show breaking of solvent structure.

G. SPECTROSCOPIC AND OTHER OPTICAL METHODS

1. Theory

The coordination and solvation numbers of ions and complexes can be obtained from displacement and change in intensity of absorption bands. For acids in water the distribution of intensity along the water band can arise from the hydration of ions. Change in shape of hypersensitive and normal absorption bands with concentration of electrolyte and temperature can be used to determine the degree of and change in solvation. The appearance of new bands and their change in intensity with temperature, electrolyte concentration, and solvent composition can be correlated with ion solvation. Rotation of polarized light and fluorescence are used in the determination of solvation.

These optical methods depend on the change in the absorption bands of valence vibrations, and the change in rotational bands of solvent and complex molecules with the nature and concentration of electrolyte, nature and composition of solvent, and temperature. The references follow for the details of theories and calculations.

2. Experimental and Results

The displacement of absorption bands and a change in their intensity caused by solvation process have been discussed.[444] Fluorescence is a very sensitive criterion for solvation.

For acids in water[445] the distribution of intensity along the water band is due to the hydration of the ions.

Assuming negligible hydration of $NaNO_3$ the study of the Raman band of water in electrolyte solutions showed HCl changes trihydral into dihydral water upon the formation of hydrates with two molecules of water.[446]

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Table XVII

Solvation of Ions Determined by Optical Methods

Method	*Solvent*	*Solvated ion*	*Solvent particles/ion*	*Ref*
Optical rotation	Methanol	Li^+	4	452
Optical rotation	Methanol	Na^+	2.2	452
Optical rotation	Methanol	K^+	1.2	452
Optical rotation	Methanol	Cl^-	1	452
Optical rotation	Methanol	I^-	0	452
Optical rotation	Acetophenone	Li^+	1	452
Optical rotation	Acetophenone	Na^+	0.5	452
Optical rotation	Acetophenone	K^+	0.5	452
Optical rotation	Acetophenone	Cl^-	0	452
Optical rotation	Acetophenone	I^-	0	452
Absorption spectroscopy	Water	Cu^{2+}	4	458
Absorption spectroscopy	Water	Nd^{3+}	3	458
Absorption spectroscopy	Water	Co^{2+}	6	458
Absorption spectroscopy	Water	VO^{2+}	5	475
Spectrophotometric	Water	Cu^{2+}	6	476
Spectrophotometric	Water–acetone	Cu^{2+}	$4H_2O$–$2(CH_3)_2O$	476
Spectrophotometric	Water–EtOH	Cu^{2+}	$4H_2O$–2EtOH	476
Absorption spectra	Water	Nd^{3+}	6	495
Absorption spectra	Water–MeOH	Nd^{3+}	$4H_2O$–2MeOH	495
Absorption spectra	Water–MeOH	Nd^{3+}	$2H_2O$–4MeOH	495
Absorption spectra	Methanol	Nd^{3+}	6	495
Absorption spectra	Water	Nd^{3+}	9	498
Absorption spectra	Water	Nd^{3+}	8	498

A Raman study of salts and acids in water showed that the change in water equilibrium is due to anions, and changes in band structure are due to hydration of cations.[447]

Electrical conductance and viscosity indicate that Mg^{2+} and Li^+ ions are relatively small and more hydrated than is usual for ions.[448] Spectral data was not definitive.

The effects of the ions Cl^-, Br^-, I^-, NO_3^-, ClO_3^-, ClO_4^-, IO_4^-, CO_3^{2-}, and SO_4^{2-} on the structure of water were studied using Raman spectra.[449] It was found that the first maximum of water (~3200 cm^{-1}) is, except for ClO_4^-, SO_4^{2-}, CrO_3^{2-}, and IO_3^-, considerably weakened. In contrast the second band at ~3400 cm^{-1} is much strengthened. For KCl the 3400-cm^{-1} maximum is doubled and the 3200-cm^{-1} invisible. A new maximum occurs at 3600 cm^{-1} with perchlorates. The effects of electrolytes and of temperature on water are quite different, and the proposed similarity of these effects must be discarded.

From the optical rotation in water and 2 *M* solution of KCl of the salt of molybdic acid and malic acid of the type $[4MoO_3\cdot 2C_4O_5H_4](NH_4)_4$, it was found that 1 mol of KCl binds 14 mol of water.[450] The rotation $[\alpha]_c$ approached a limiting value, $[\alpha]_{lim}$. In the equalibrium

$$[4MoO_3\cdot 2C_4O_5H_4]^{4-} + H_2O \rightleftharpoons [4MoO_3O]^{2-} + 2C_4O_5H_5^-$$

the ion $C_4O_5H_5^-$ has little effect on light rotation. From the ratio $[\alpha]_c/[\alpha]_{lim}$ in water and KCl, the extent of hydration of KCl was found.

Using the method described by Darmois,[451] the solvation of ions (Table XVII) in methanol and in acetophenone was found[452] from light rotation. In this method Stoke's law is used to calculate the radius of the ion and from this its real volume. Another additive part obtained from the densities of the solutions is used in obtaining the apparent volume of the ions. Extrapolated to infinite dilution the apparent volume at most equals the real volume. If they are not equal, the apparent volume is adjusted by adding to the volume on *n* molecules of solvent so as to equal the real volume. Thus one obtains the solvation number *n* of the ion.

Microwave absorption studies were made of water–salt equilibrium.[453] In a solution of NaCl in 10% water at −10° the rate of absorption decreases with time until the reaction NaCl + solution $\rightarrow$ $NaCl\cdot 2H_2O$ is completed.

Light absorption by a single ion depends critically on the configuration of the adjoining polarized medium.[454] The role of this configuration in electronic transitions involving one or a pair of ions is treated applying Debye's "diffusion" theory for ion collision rates and a nonadiabatic type of potential curve. Rates of chemical processes depend decisively on the interaction of two ions at separations where the Coulombic law is not valid.

Specific refraction was used to study solvation.[455] An equation was formulated relating specific refraction, *r*, of a solution to concentration, *c*, of the dissolved substance as functions of the specific refractions of dissolved substance, *R*, and of the solvent, *R'*. If *m* moles of solvent solvates 1 mol of solute, *mc* is substituted for *c* for the solvated molecule, and $1 - c - mc$ = concentration of free solvent. *R'* and *r* are calculated from densimetric and refractometric measurements. Solving the resulting equations showed that *r* did not depend on *c*, and almost equals *R'*. Four mathematical identities followed from this. If *r* is known for any two neighboring concentrations, the values *R* and *R''* and finally *m*

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for any solution can be calculated. R'' is the specific refraction of dissolved ions.

Adsorption spectra of alcohol–water solutions of $CuCl_2$ were used to determine the number of water molecules in the water–ethanol envelope of the Cu^{2+} ion.[456] The $CuCl_2$ was dissolved in alcohol and water added for the absorption spectra study. The number of water molecules in the ionic envelopes was calculated from derived transcendental equations. The equations were linear at a high ratio of water to copper ions. Two water molecules were present in the mixed EtOH–H_2O envelope of Cu^{2+} ions.

The solvation of anhydrous neodymium chloride in ethanol to which water was added was investigated by absorption spectrometry.[457] When there was insufficient water to hydrate all of the Nd^{3+} ions, they were solvated by both EtOH and H_2O. For complete displacement of EtOH molecules of solvation 20–30 molecules of water per Nd^{3+} ion were required because of the slightly greater solvation energy with EtOH than with H_2O.

The adsorption spectrum of the anhydrous chlorides of Co^{2+}, Cu^{2+}, and Nd^{3+} ions in EtOH–H_2O were used to determine their hydration[458] (see Table I).

The spectral measurement of a liquid phase above its normal boiling point suggested an effect of temperature on the solvation sphere of NpO_2^+ and a concomitant interaction of NO_3^- ion with the NpO_2^+–solvate system.[459]

In methyl alcohol solutions of HCl a line observable at low dilutions appeared which indicated the formation of the compound MeOH·HCl and arose from the oscillation of the MeOH·HCl bond.[460]

Shifts covering more than 20 kcal of the ultraviolet absorption band of the solvated iodide ion at 2200 Å were observed for changing environment involving various pure and mixed solvents and salts which did not absorb strongly in this region and for changing temperature.[461,462] These large and characteristic shifts are common to all negative ions absorbing by a charge-transfer-to-solvent mechanism.

From infrared spectroscopy of water in nonaqueous solutions of uranyl nitrate, it was determined that 2 mol of water in $UO_2(NO_3)_2 \cdot 6H_2O$ are in a state of marked deformation due to the stable bonds between the water and the $UO_2(NO_3)_2$.[463] The nature of the solvent determines the degree of deformation. In organic solvents the remaining moles of water in $UO_2(NO_3)_2 \cdot 6H_2O$ are deformed to a lesser degree and are less tightly bound.

The Raman-active vibration frequencies in dilute solutions of $HgCl_2$, in various solvents, were all less than that for the gas.[464] The relative change in frequency was roughly linear with the dielectric constant of the solvent for other bonds with partial ionic character. The ionic character of the Hg–Cl bond was about 28%, in fair agreement with that from the bond dipole moment.

The effect of environmental changes on the ultraviolet spectrum of iodide ion in pure and mixed solvent was studied. The first electronic band at 200–50 mμ of solvated I^- was observed over a range of temperatures.[465] The data on band maxima molar extinction coefficients and temperature coefficients agreed with a square-well model of the excited state. No complex formation between I^- and solvent was indicated in mixed solvents. The best model consisted of excited electrons confined to the first layer of solvent molecules.

From refractive index and density measurements on strong electrolytes in solutions, the hydration numbers of electrolytes and the polarizability of the water molecules were obtained.[466] These hydration numbers were divided into primary and secondary hydration numbers (Table XVIII).

Table XVIII

Primary and Secondary Over-All Hydration Numbers for Some Uni-univalent Electrolytes[a]

	Over-all hydration no.		
Electrolyte	*Primary*	*Secondary*	*Ref*
NaCl	6	28	466
NaBr	6	26	466
KCl	5	34	466
KBr	5	22	466
KI	5	19	466

[a] These were found to be nearly independent of temperature.

From shifts and broadening of the absorption bands for Cu^{2+} and CO^{2+} salts in alcohol solutions upon the addition of water, ions exist which are simultaneously solvated by molecules of water and of alcohol.[467] The maximum values for hydration numbers were 6.

Studying the effect of the solvent on the electron spectra of phthalimides, it was found that the action of the solvent on the electron-vibration levels of solute molecules increases with increasing complexity and with the intensification of intermolecular interaction in the medium.[468]

From absorption spectra of alcohol–water solutions Cu^{2+} ion shows a strong tendency to be solvated with alcohol rather than with water.[469]

Optical absorption spectra of ions in water, methanol, and ethanol solutions showed that all the solvates formed in the cases of $Cu(NO_3)_2 \cdot 3H_2O$ and $CuCl_2 \cdot 2H_2O$ had similar structure, which changed strongly with concentration only for $CuCl_2$ in water and methanol.[470] A higher intensity of field was created by alcohol than by water molecules as shown by the difference in forces of oscillators in the two solvents. The ligands distribute themselves around the Cu^{2+} ion with the symmetry of a tetragonal bipyramid.

Absorption spectra studies of Ti^{3+} ion in aqueous solutions indicated that in dilute solutions the hydrates formed had a

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D_{4h} tetragonal-bipyramidal[471] symmetry. The changes in spectra at high Ti^{3+} concentrations were due to penetration of the Cl^- ion into the Ti^{3+} shell.

Unchanged spectra indicated that $FeCl_3$ and $CuCl_2$ solvates in dimethyl sulfoxide solutions were not affected by excess alkali chloride.[472] However, excess alkali chloride causes $CoCl_2$ to form $CoCl_4^{2-}$, which could be changed to the solvate by chloride acceptors $ZnCl_2$ and $HgCl_2$ in 2:1 concentration, but completely restored by KCl when the ratio $CoCl_2$:MCl_2:KCl became 1:2:4.

Optical absorption spectra were used to study the solvation of CO^{2+} and Cu^{2+} ions in solutions of methanol, ethanol, acetone, and methyl ethyl ketone.[473] In all solvents with no chloride ion present, the Co^{2+} ion had octahedral symmetry, and in methyl alcohol it had this symmetry with dilute Cl^- present. In methanol with concentrated Cl^- and in ethanol with any Cl^- ion, two chloride ions replaced two solvent molecules in the cis position giving a rhombic complex. Methanol solvated Co^{2+} ion more strongly than did ethanol. In acetone and methyl ethyl ketone the solvated Co^{2+} ion showed tetragonal symmetry at all Cl^- concentrations with one or two Cl^- ions in the trans position. The solvated Cu^{2+} complex showed tetragonal-bipyramidal symmetry in all solutions with no Cl^- and in alcohol with low Cl^- concentration and likewise with appreciable concentration of Cl^- but in this case consisted of a Cl^- and two solvent molecules in the trans position. In acetone and methyl ethyl ketone solutions containing any Cl^-, the complex had rhombic symmetry with two chlorides in the cis position.

The onset of the absorption band of I^- ion was investigated using 15 anions of various types and valencies.[474] The spectrographic effect of anions depends on their power to dehydrate the test ion, I^-. Complex ions such as citrate, tartrate, and phosphate ions show larger effects than halide ions. At like concentrations, citrate ion shows ten times the effect of bromide ion.

Optical spectra were used to investigate the hydration of the vanadyl ion in aqueous solutions as functions of $VOCl_2$ and of Cl^- ion concentrations.[475] In the presence of an excess of Cl^- ion, $VOCl_5^{3-}$ was formed; otherwise $VO(H_2O)_5^{2+}$ was produced. The hydrates and the solvates both had the same C_{4v} symmetry. The solvation of VO^{2+} differed from those of Ti^{3+} and Cu^{2+} because of the presence of the V–O bond.

Spectrophotometric measurements were made of $Cu(NO_3)_2$ and $Cu(ClO_4)_2$ in acetone–water and ethanol–water solutions.[476] The marked increase in the visible region of the extinction coefficients with decrease in water concentration is due to the successive replacement of the two water molecules of the Cu^{2+} hydration sphere by two acetone or alcohol molecules. The equilibrium constants for the first replacement are 3.7 and 1.8 and for the second replacement 3.1×10^{-3} and 3.1×10^{-2} for acetone and ethanol, respectively. Ligand field strength can account for the small deviation of the first constants from statistical expectation, but not for the small values of the second constants, which are apparently depressed by a general solvent effect.

In the ultraviolet spectrum of iodides in dioxane–water mixtures, the shift in wavelength of maximum absorption for Bu_4NI was attributed to replacement of water molecules around the I^- ion by dioxane as the mole fraction of dioxane increases, and is regarded as equivalent to an increase of an excited electronic orbital[477] due to the presence or absence of solvent molecules between ions of the ion pair.

Equilibrium between violet and green CrK alums as a function of time was studied using visible spectra.[478] At equilibrium both gave identical adsorption spectra. It was supposed that two processes, hydration–dehydration and hydrolysis, came to equilibrium in solutions of these alums.

The copper(II) and cobalt(II) chlorides and nitrates were examined using optical absorption spectra in the solvents water, methanol, ethanol, acetone, and methyl ethyl ketone.[479] The bond strengths are, in the order Cu^{2+}–Cl^- = Cu^{2+}–solvent; Co^{2+}–H_2O > Co^{2+}–Cl^- = Co^{2+}–ROH > Co^{2+}–ketone.

Nitrates of copper, zinc, mercury, and indium, sulfates of copper, magnesium, zinc, gallium, indium, and thallium, and perchlorates of copper, mercury, indium, and magnesium were studied by Raman spectroscopy in nearly saturated aqueous solutions.[480] All bivalent ions except copper gave lines indicating the formation of hexacoordinated aquo complexes. Higher intensities and frequencies for gallium and indium than for other metal complexes indicate stronger bonding of hydration sheaths due to increased ionic charge. The comparatively greater viscosities of the gallium and indium solutions confirm the greater solvation.[481,482]

A comparison has been made of the infrared spectra of a hydrate with a full coordination shell of water, of lower hydrates, and of anhydrous salt.[483]

Salt effects on aqueous solutions from infrared bands of water were used to show secondary hydration of ions, up to several hundred water molecules per pair of ions.[484]

The stepwise displacement of two water molecules of solvation by acetone and by ethanol in Co^{2+} and Ni^{2+} ions was found from visible absorption spectra of cobalt(II) perchlorate and nickel(II) perchlorate.[485] It is concluded that the low values of the equilibrium quotients may arise from both a thermodynamic trans effect and a general solvent effect.

Bound water was determined in electrolyte solutions by absorption spectrometry in the near-infrared.[486] In salts forming hydrates, bound water corresponds to water of crystallization; however, bound water was also found in nonhydrated salts.

Absorption spectra of the water–organic solvent–salt ternary system have been investigated.[487] When lithium, mag-

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nesium, and aluminum perchlorates were added to H_2O–methyl ethyl ketone or D_2O–methyl ethyl ketone, solvation of the cation or anion was indicated by characteristic shifts. These depended on solvent composition.

The Raman and infrared studies of aqueous calcium nitrate solution as well as mixtures involving high Ca^{2+} to NO^{3-} or NO_3^- to Ca^{2+} concentrations have been observed.[488] The removal of the degeneracy of the E′ modes, and the activity of the A′ modes suggested that the symmetry of the NO_3^- ion had been lowered by solvation with water. The perturbation was advanced by ionic interaction with hydrated Ca^{2+} ions. A model was proposed.

The effect of various ions on the infrared spectra of water in crystal hydrates and solutions, and of water on the infrared absorption of ions containing oxygen, have been investigated.[489] Water of crystallization forms hydrogen bonds with anions containing oxygen. The bonds become weaker on going from crystal hydrates to solutions. Al^{3+}, Cr^{3+}, Be^{2+}, Zn^{2+}, Li^+, SO_4^{2-}, OH^-, and F^- increased while Ca^{2+}, K^+, ReO_4^-, ClO_4^-, I^-, NO_3^-, and SCN^- weakened the strength of the bonds.

The ratio of water to acetate ion in the solvation shell of europium(III) and of terbium(III) as a function of acetate concentration was examined using the fluorescence intensity and lifetimes of Eu^{3+} and Tb^{3+} in water and in deuterium oxide solutions.[490] For the ratio of water to acetate ion found which agreed with those found by Sonesson[491,492] by potentiometric measurements, the ratio of the hydration number in pure water to the number of water molecules replaced by each acetate ion must be 6.

From the infrared spectra of the Al^{3+} and Sc^{3+} salts of polystyrenesulfonic acid, foils of polyelectrolytes under quasi-liquid conditions incorporated the molecules of hydration directly between cation and adjacent anion.[493] First two and then more layers of water molecules occur between cation and anion at higher degrees of hydration.

Thorium(IV) complexes with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (TTA) and *o*-phenanthroline (phen), namely, Th(TTA)$_4$(phen) and Th(TTA)$_4$(1,1′-bipyridyl), were found by spectroscopy to have coordination numbers of 10.[494]

The compositions (Table XVII) and stabilities of neodymium solvates in water–methyl alcohol solutions were studied.[495] The higher the MeOH concentration, the greater the number of methanol molecules substituting for water in the ion solvation sheath.

Up to 540° the spectra in certain regions of uranium(IV) and uranium(III) in molten fluoride compared to their spectra in other molten salt systems suggested that the coordination number of the uranium species in the molten fluoride is possibly 8 or 9.[496]

The interaction of ions with the nearest water molecules in an organic medium was spectrographically investigated in solutions of the perchlorates of Na^+, Li^+, Mg^{2+}, and Co^{2+} and iodides of Na^+, Li^+, and $(C_4H_9)_4N^+$ in acetone or methyl cyanide containing semiheavy water ($H_2O + D_2O$).[497] From the changes in the absorption bands of valence vibrations, the interactions of the ions with the nearest water molecules could be studied in the absence of water–water hydrogen bonds. A new band appeared in the absorption spectrum due to the hydroxyl group in methyl cyanide solutions. The intensity of the new band increased with increasing salt concentration. The magnitude of the new band shifted in the order $NaClO_3 < LiClO_3 < Mg(ClO_3)_2 < Co(ClO_3)_2$. Presumably the new band was due to hydrated complexes of the type $M^{n+}\cdots O(D)H\cdots N{\equiv}CMe$. A third band of lower frequency appeared in iodide solutions, perhaps from complexes of the type $M^{n+}\cdots O(D)H\cdots I^-$. A similar study was made of deuteroxyl absorption spectra in methyl cyanide and acetone solutions of the same salts.

Optical properties of rare earth complexes including fluorescence and luminescence were discussed and experimental proofs compiled for coordination numbers greater than 6 in rare earth complexes.[498] Proofs were given for the high coordination number of lanthanides in chelates with polyaminocarboxylic acids and in β-diketone complexes.

By comparison with absorption spectra of nine- and eight-coordinated Nd^{3+}, the shape change in aqueous Nd^{3+} spectra was interpreted as a change in coordination number of the aquo Nd^{3+} from 9 in dilute solutions to 8 in concentrated solutions (Table I). It was assumed that other normally nine-coordinated lanthanide ions undergo a similar change. In concentrated chloride all lanthanide ions are perhaps eight-coordinated, possibly $Ln(H_2O)_8{}^{3+}$ ions. In strong chloride solutions, trivalent actinide ions were thought to be chlor complexes.

Correlations were investigated between the solvation numbers of ions and the characteristics of the rotational Brownian movement of the molecules of the solvent, namely, relaxation time of reorientation, τ, and the coefficient of the rotational diffusion, D_r, in nonaqueous solutions of electrolytes. A complete correlation was found between the change in the solvation number and the change in the total interaction between the ions and molecules of the solvent and the time of relaxation of reorientation τ as well as D_r.[499] The smallest ions as Li^+ have the greatest solvation numbers and exert the greatest inhibiting effect on methanol molecules. Of several alcohols Li^+ and Cl^- ions exerted the greatest inhibiting effect on methanol molecules and the least on amyl alcohol molecules.

3. Significance

The optical methods are accurate, comparatively rapid, and do not involve alteration of the sample. Spectroscopy allows observations on the individual components of a sample rather than on the composite sample, since the bond and rotational frequencies are characteristic parameters for each component. Structural features of the sample are determinable using spectroscopic and other light-measuring approaches. Spectral studies are not definitive in all cases. The spectroscopic approach has shown that the effects of electrolytes and

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temperature on water, assumed to be the same, are quite different.

H. SOUND VELOCITY. COMPRESSIBILITY

1. Theoretical

The adiabatic compressibility, β_a, of a liquid is related to the velocity, v, of sound in cm/sec for a liquid of density ρ, g/ml, by the equation[500,501]

$$\beta_a = 10^6 v^{-2} \rho^{-1} \text{ bar}^{-1} \tag{80}$$

From β_a the isothermal compressibility, β, can be calculated

$$\beta = \beta_a \frac{C_p}{C_v} = \beta_a + \frac{\alpha^2 T}{J C_p \rho} \tag{81}$$

where C_p and C_v are the heat capacities and α is the coefficient of volume expansion. Substituting $(-1/\rho)\mathrm{d}\rho/\mathrm{d}T$ for α in eq 81 yields

$$\beta = \beta_a + \{[(\mathrm{d}\rho/\mathrm{d}T)_p]^2 T\}/\rho^3 J C_p \tag{82}$$

By proper substitution eq 82 was put in the form

$$\beta = \beta_a + 0.07125(\rho_{30^\circ} - \rho_{20^\circ})/(\rho_{25^\circ})^3 C_p \tag{83}$$

The decrease in compressibility of electrolyte solutions with increasing electrolyte concentration was explained[502] by assuming that the solvent molecules solvating ions were fully compressed by the electrical forces of the ions and in the primary solvent shells of the ions were rendered incompressible. The adiabatic compressibilities of solution, β_a, and that of solvent, $\beta_{0,a}$, were related by the equation

$$\beta_a + \beta_{0,a} = \left(1 - S\frac{n_2}{n_1}\right) \tag{84}$$

where S is the primary solvation number of the electrolyte and n_1 and n_2 are the numbers of moles of solvent and solute present, respectively. By extrapolation of the graph of S *vs.* n_2 to $n_2 = 0$, "true" solvation numbers, S_0, may be obtained.

Allam and Lee[500] expressed the compressibilities of electrolytes in water, methanol, and ethanol by the equation

$$\beta_a = \beta_{0,a}[1 + n_2(S_0 + An_2 + Bn_2^2)/n_1] - 1 \tag{85}$$

where A and B are constants, and the remaining terms have been defined. The equation reproduced the data observed. Equation 85 was used to obtain the limiting solvation numbers of various electrolytes at 25° in water, methanol, and ethanol.

Assuming an incompressible solvation shell plus a central ion model, an entirely different method has been adopted[502–506] to give a parameter of hydration. The model gives the volume of water, V_h, bound to 1 mol of solute in solution reduced to 1 atm of pressure, P_0, to be

$$V_h = (n_1\beta_1^{(p_0)} V_1^{(p_0)} - \beta^{(p_0)} V^{(p_0)})/\beta_1^{(p_0)} = -K_2/\beta_1^{(p_0)} \tag{86}$$

where n_1 is the number of moles of water in the solution, β_1 the isothermal compressibility of the water, V_1 the molar volume of water, β the isothermal compressibility of the solution, and K_2 the apparent molal compressibility of the solute; $P_0 = 1$ bar.

Using compressibility and density data, the value of V_h may be calculated. The average hydration number, h, of a pair of solute ions can be calculated using the equation

$$h = V_1/V_h^{(p_0)} \tag{87}$$

Several authors[502–508] have attempted to evaluate V_h and h.

2. Experimental Technique

Compressibility was used to obtain solvation numbers of ions.[500–509] From the wavelengths of the ultrasonic waves the ultrasonic velocities in solvents and solutions have been calculated, and from these and measured densities the adiabatic and isothermal compressibilities obtained for the solvents and solutions. From the compressibilities of pure solvent and solutions hydration numbers of the electrolytes were obtained.[500–508] Then making an assumption concerning the solvation number of some particular ion, the solvation numbers of various ions have been calculated.

3. Solvation Numbers Found

In Table XIX are presented the limiting solvation numbers of electrolytes at infinite dilution, and in Table XX are listed the solvation numbers of individual ions, assuming that in water solvent the hydration numbers of K^+ and Cl^- ions in KCl are equal, and of ions assuming that in water, methanol, and ethanol the nitrate ion has two solvent molecules of solvation.

In Table XX are presented average hydration numbers for electrolytes (ion pairs). Multiple temperatures and multiple values of the average hydration numbers at these different temperatures are enclosed in parentheses.

Tables XIX and XX contain[510] respectively hydration numbers at infinite dilution of some acids, alkalis, and tetraalkylammonium salts, and the limiting hydration numbers of the ions involved assuming the planar nitrate ion can hold two water molecules in its primary hydration shell,[500–511] all at 25°.

The solvation of ions (Table XX) was found from compressibility of solutions obtained from the velocity of ultrasonic waves in them.[512–516] The mathematical theory was developed relating the degree of solvation of an electrolyte to the compressibility of its solution.[512]

Adiabatic compressibility studies of aqueous electrolyte solutions showed that the structure of water became more highly coordinated and compacted with the introduction of ions.[517]

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Table XIX

Solvation Numbers of Electrolytes

Method[a]	*Electrolyte*	*Solvent*	*Temp, °C*	*Concn*	*Solvn no.*	*Ref*
AC	NaOH	Water	25	0	9.9	500
AC	KOH	Water	25	0	9.2	500
AC	LiOH	Water	25	0	8.7	500
AC	NaCl	Water	25	0	7.1	500
AC	KCl	Water	25	0	6.4	500
AC	LiCl	Water	25	0	6.0	500
AC	NH_4Cl	Water	25	0	4.2	500
AC	$MgCl_2$	Water	25	0	12.5	500
AC	$MgSO_4$	Water	25	0	14.8	500
AC	$NaNO_3$	Water	25	0	6.9	500
AC	KNO_3	Water	25	0	6.1	500
AC	$AgNO_3$	Water	25	0	6.0	500
AC	$LiNO_3$	Water	25	0	5.6	500
AC	NH_4NO_3	Water	25	0	4.1	500
AC	NaBr	Water	25	0	6.5	500
AC	KBr	Water	25	0	5.9	500
AC	LiBr	Water	25	0	5.4	500
AC	NH_4Br	Water	25	0	5.7	500
AC	NaI	Water	25	0	6.0	500
AC	KI	Water	25	0	5.4	500
AC	LiI	Water	25	0	4.7	500
AC	NH_4I	Water	25	0	3.2	500
AC	NaI	Methanol	25	0	6.2	500
AC	KI	Methanol	25	0	6.0	500
AC	LiI	Methanol	25	0	5.6	500
AC	NH_4I	Methanol	25	0	5.5	500
AC	$NaNO_3$	Methanol	25	0	5.9	500
AC	$LiNO_3$	Methanol	25	0	5.3	500
AC	NH_4NO_3	Methanol	25	0	5.2	500
AC	NaBr	Methanol	25	0	5.6	500
AC	KBr	Methanol	25	0	5.2	500
AC	LiBr	Methanol	25	0	5.0	500
AC	NH_4Br	Methanol	25	0	5.0	500
AC	NaCl	Methanol	25	0	4.7	500
AC	LiCl	Methanol	25	0	4.2	500
AC	NH_4Cl	Methanol	25	0	4.9	500
AC	LiI	Ethanol	25	0	3.7	500
AC	NaI	Ethanol	25	0	3.2	500
AC	NH_4I	Ethanol	25	0	3.3	500
AC	$LiNO_3$	Ethanol	25	0	3.4	500
AC	NH_4NO_3	Ethanol	25	0	2.9	500
AC	LiBr	Ethanol	25	0	3.4	500
AC	NaBr	Ethanol	25	0	2.9	500
AC	NH_4Br	Ethanol	25	0	2.5	500
AC	LiCl	Ethanol	25	0	2.7	500
AC	LiCl	Water	25		4.24	506
AC	$LiNO_3$	Water	25		2.98	506
AC	NaCl	Water	20 (25)		5.96 (4.98)	506
AC	NaBr	Water	20		4.82	506
AC	NaI	Water	20		3.37	506
AC	NaOH	Water	25		8.40	506
AC	KCl	Water	20 (25)		5.17 (4.41)	506
AC	KBr	Water	20		3.97	506
AC	KI	Water	20		2.92	506
AC	$(C_2H_5)_4NBr$	Water	25		10.4	510
AC	NH_4Br	Water	25		3.7	510
IC	NaCl	Water	25		5.70	550
IC	KCl	Water	25		5.0	550
IC	NaBr	Water	25		4.3	550
IC	KBr	Water	25		3.8	550
IC	NaI	Water	25		3.4	550
IC	KI	Water	25		2.6	550
IC	$MgCl_2$	Water	25		11	550
IC	$SrCl_2$	Water	25		13	550

Table XIX (Continued)

Method[a]	*Electrolyte*	*Solvent*	*Temp, °C*	*Concn*	*Solvn no.*	*Ref*
IC	Na_2SO_4	Water	25		18	550
IC	$MgSO_4$	Water	25		17	550
AC	NH_4Cl	Water	25		1.50	506
AC	$MgCl_2$	Water	20 (25)		11.8 (10.4)	506
AC	$Mg(NO_3)_2$	Water	25		8.38	506
AC	$CaCl_2$	Water	20		11.3	506
AC	$Ca(NO_3)_2$	Water	25		7.60	506
AC	$BaCl_2$	Water	20 (30) (40)		12.6 (11.4) (11.1)	506
AC	Na_2CO_3	Water	20 (25)		19.1 (15.7)	506
AC	Na_2SO_4	Water	20		18.2	506
AC	K_2SO_4	Water	25		14.4	506
AC	$(NH_4)_2SO_4$	Water	25		9.34	506
AC	$MgSO_4$	Water	25		14.7	506
AC	$CuSO_4$	Water	25		13.2	506
AC	NaOH	Water	25		9.9	510
AC	KOH	Water	25		9.2	510
AC	LiOH	Water	25		8.7	510
AC	HCl	Water	25		2.1	510
AC	HNO_3	Water	25		1.8	510
AC	CH_3COOH	Water	25		1.8	510
AC	$(CH_3)_4NBr$	Water	25		6.7	510

[a] AC = adiabatic compressibility; IC = isothermal compressibility.

The absorption of sound[518] by aqueous solutions of electrolytes was investigated for frequency, concentration, and temperature dependence. Uni-univalent and bi-bivalent electrolytes showed no absorption except for higher concentrations of Na_2SO_4 and $MgCl_2$. The bi-bivalent sulfates showed great absorption which from the slope of the frequency response was due to the relaxation process. For $MgSO_4$ the dependence on concentration proved linear; this indicates a constant absorption cross-section per mole. The further increase above 5 Mc/sec was possibly due to another relaxation process caused by a change in the hydration shells of the reacting ions.

Adiabatic compressibility of gelatin sol[519] and aqueous solutions of sugars[520] and of dicarboxylic and hydroxycarboxylic acids[521] were made. It was found that a molecule of monosaccharide combined with four molecules of water as expected if each OH group hydrogen bonded with a molecule of water. A polysaccharide molecule also combined with four molecules of water. Apparently some of the sugar OH's hydrogen bonded with each other, and thus could not bond with water. The adiabatic compressibility data for maleic anhydride and of malonic, succinic, glutaric, oxalic, tartaric, citric, and malic acids perhaps arose from hydration effect of radicals. The negativity of the methylene coefficient was attributed to the radicals' hydrophobic nature.

Ultrasonic absorption studies on electrolyte solutions have been made and a bi-bivalent relaxation maximum was found,[522] the frequency of which was independent of concentration, but depended on the metal ion, and increased with temperature. Hydration, association, dissociation, and hydrolysis mechanisms were used to explain the data. Only the hydrolysis mechanism explained all the observed facts.

From the speed of ultrasonic waves in solutions of sucrose, galactose, arabinose, maltose, and lactose, 2 mol of water was linked to each OH group in the carbohydrate molecule.[523]

Ultrasonic interferometer hydration studies indicated the mean pressure of hydration to be 4000 atm provided that water of volume V is compressed by ΔV owing to hydration.[524]

From compressibilities, solvation numbers of ions at infinite dilution were determined (Table XX).[525] Assuming the solvation layer had negligible compressibility, the solvation numbers were calculated. Ultrasonic studies of hydration–dehydration in polyelectrolyte solutions were made.[526] Hydration was determined for methacrylic and polyacrylic solutions which were progressively neutralized by NaOH and Bu_4NOH.

From ultrasonic velocity in nitrate solutions, it was found that the larger the ionic radius the greater the hydration.[527] The relation of the compressibility of aqueous solutions of electrolytes with common anions to the ionic size of the cation was explained by a dependence on hydration and charge of the ions.[528]

Ultrasonic absorptions of aqueous zinc acetate as a function of temperature passed through a maximum.[529] This was explained on the basis of chemical relaxation and formation of an activated complex with an activation energy of 4.38 kcal/mol. With solutions above 0.05 N the reaction is

$$Zn(OAc)_2 + nH_2O \longrightarrow Zn(OAc)_2(H_2O)_n \qquad (88)$$

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Table XX

Solvation Numbers of Ions by the Method of Adiabatic Compressibility

Solvent	*Ref ion*	*Solvn no. of ref ion*	*Concn*	*Temp, °C*	*Solvated ion*	*Solvn no. of solvated ion*	*Ref*
Water	K^+ or Cl^-	3.2	0	25	Na^+	3.9	500
Water	K^+ or Cl^-	3.2	0	25	Li^+	2.7	500
Water	K^+ or Cl^-	3.2	0	25	NH_4^+	1.1	500
Water	K^+ or Cl^-	3.2	0	25	Ag^+	3.1	500
Water	K^+ or Cl^-	3.2	0	25	Mg^{2+}	7.0	500
Water	K^+ or Cl^-	3.2	0	25	NO_3^-	2.9	500
Water	K^+ or Cl^-	3.2	0	25	Br^-	2.6	500
Water	K^+ or Cl^-	3.2	0	25	I^-	2.1	500
Water	K^+ or Cl^-	3.2	0	25	OH^-	6.1	500
Water	K^+ or Cl^-	3.2	0	25	SO_4^{2-}	8.8	500
Water	NO_3^-	2.0	0	25	Na^+	4.8	500
Water	NO_3^-	2.0	0	25	K^+	4.1	500
Water	NO_3^-	2.0	0	25	Li^+	3.6	500
Water	NO_3^-	2.0	0	25	NH_4^+	3.0	500
Water	NO_3^-	2.0	0	25	Ag^+	4.0	500
Water	NO_3^-	2.0	0	25	Mg^{2+}	7.9	500
Water	NO_3^-	2.0	0	25	Cl^-	2.3	500
Water	NO_3^-	2.0	0	25	Br^-	1.7	500
Water	NO_3^-	2.0	0	25	I^-	1.2	500
Water	NO_3^-	2.0	0	25	OH^-	5.2	500
Water	NO_3^-	2.0	0	25	SO_4^{2-}	7.9	500
Methanol	NO_3^-	2.0	0	25	Na^+	3.9	500
Methanol	NO_3^-	2.0	0	25	K^+	3.6	500
Methanol	NO_3^-	2.0	0	25	Li^+	3.3	500
Methanol	NO_3^-	2.0	0	25	NH_4^+	3.3	500
Methanol	NO_3^-	2.0	0	25	Br^-	1.7	500
Methanol	NO_3^-	2.0	0	25	Cl^-	0.9	500
Methanol	NO_3^-	2.0	0	25	I^-	2.4	500
Ethanol	NO_3^-	2.0	0	25	Na^+	0.9	500
Ethanol	NO_3^-	2.0	0	25	Li^+	1.4	500
Ethanol	NO_3^-	2.0	0	25	NH_4^+	0.9	500
Ethanol	NO_3^-	2.0	0	25	I^-	2.3	500
Ethanol	NO_3^-	2.0	0	25	Br^-	2.0	500
Ethanol	NO_3^-	2.0	0	25	Cl^-	1.3	500
Water	NO_3^-	2.0	0	25	Na^+	4.8	510
Water	NO_3^-	2.0	0	25	K^+	4.1	510
Water	NO_3^-	2	0	25	Li^+	3.6	510
Water	NO_3^-	2	0	25	Cl^-	2.3	510
Water	NO_3^-	2	0	25	Br^-	1.7	510
Water	NO_3^-	2	0	25	OH^-	5.2	510
Water	NO_3^-	2	0	25	$(CH_3)_4N^+$	5.0	510
Water	NO_3^-	2	0	25	$(C_2H_5)_4N^+$	8.7	510
Water	NO_3^-	2	0	25	NH_4^+	2.0	510
Water					H^+	1–2	512
Water					Li^+	5–6	512
Water					Na^+	6–7	512
Water					K^+	6–7	512
Water					Mg^{2+}	16	512
Water					Ba^{2+}	16	512
Water					Be^{3+}	8	512
Water					Al^{3+}	31	512
Water					F^-	2	512
Water					Cl^-	0–1	512
Water					Br^-	0	512
Water					I^-	0	512
Water					Li^+	2	525
Water					Na^+	3	525
Water			0		K^+	2	525
Water			0		Cs^+	1	525
Water			0		NH_4^+	0	525
Water			0		Mg^{2+}	8	525
Water			0		Ca^{2+}	8	525
Water			0		Ba^{2+}	8	525

Table XX (Continued)

Solvent	*Ref ion*	*Solvn no. of ref ion*	*Concn*	*Temp, °C*	*Solvated ion*	*Solvn no. of solvated ion*	*Ref*
Water			0		Cd^{2+}	5	525
Water			0		Cu^{2+}	5	525
Water			0		Zn^{2+}	6	525
Water			0		Be^{2+}	1	525
Water			0		Ce^{3+}	13	525
Water			0		OH^-	8	525
Water			0		Cl^-	3	525
Water			0		Br^-	2	525
Water			0		I^-	0	525
Water			0		CH_3COO^-	4	525
Water			0		NO_3^-	1	525
Water			0		CNS^-	0	525
Water			0		HCO_3^-	2	525
Water			0		CrO_4^-	13	525
Water			0		CO_3^{2-}	15	525
			0		SO_4^{2-}	11	525

From densitometric studies on solutions containing two electrolytes, densities of packing of the systems KCl–NaCl–H_2O and KCl–KF–H_2O were calculated.[530] NaCl added to KCl solution caused a tighter packing of hydrated ions compared to that in pure KCl solution, but KF loosened the packing greatly. H^+ decreases the volume gap among hydrated ions.

From ultrasonic studies of aqueous solutions of the nitrates of Li, Ag, Be, Ca, Cd, UO_2^{2+}, Al, and La, the hydration numbers were found for the electrolytes and compared with data from other methods.[531]

The hydration number and other ultrasonic parameters of the nitrates of Li, Ca, Cu, Mg, Mn, Ni, Zn, Fe, Al, and Cr were determined from ultrasonic velocity data.[532]

Ultrasonic studies of the hydration of NaCl, KCl, K_2CO_3, and $BaCl_2$ in mixtures of ethanol–water were made,[533] and the hydration numbers of $CaI_2 \cdot 4H_2O$ and $Th(NO_3)_4 \cdot 4H_2O$ were determined.[534]

Ultrasonic velocities and compressibilities yielded total hydration numbers as functions of concentration in solutions of $Na_2MoO_4 \cdot 2H_2O$, $Na_2CrO_4 \cdot 10H_2O$, K_3PO_4, $KHCO_3$, $Ca(HCO_3)_2 \cdot H_2O$, and CaI_2.[535] In general, the hydration decreased with increasing cationic radius except for LiOH, $Be(NO_3)_2$, and $Ca(NO_3)_2$. H_2SO_4 gave very high, HNO_3 and HCl gave very low, and NH_4OH gave negative hydration numbers.

Data on the apparent volumes and compressibilities of ions in aqueous solutions showed that the assumption of equal hydration of anions and cations is incorrect.[536] The apparent incompressible volumes of ions increased with decreased ionic radius, especially for anions.

Ultrasonic velocities were obtained in aqueous solutions of the sulfates of Li, Mg, Cd, Co, Ni, Fe, Cr, Mn, and Al.[537] From the data hydration numbers and other properties were calculated. The variation of adiabatic compressibility with concentration was inversely dependent on hydration number.

The solvation approach was used to interpret ion–solvent interaction.[538]

By the method of ultrasonic interferometry the hydration numbers for NaCl, RbCl, LiCl, KCl, CsCl, $SrCl_2$, $NiCl_2$, $BaCl_2$, $CoCl_2$, $MgCl_2$, $MnCl_2$, $CaCl_2$, $ZnCl_2$, and $CuCl_2$ in aqueous solutions and their dependence on temperature in the range 20–40° were determined.[539] The idea of clathrates as hydration shells was supported.

The spin-lattice relaxation time for protons for solutions of $CoCl_2$, $CuCl_2$, and LiCl were measured as a function of the number of moles of water per mole of solvent in aqueous methanol as water was added to the solution.[540] At higher proportions of water there was a basic structural change in the first coordination sphere as the alcohol shell was completely replaced by the hydrate shell. The filling of cation and anion influence spheres occurred in a set sequence in relation to their solvation energies.

Ultrasonic measurements yielded the hydration numbers and other properties of solutions of the chlorides of Li, Al, Cu, Cd, Mn, Mg, Ca, Ni, Co, and Sr.[541]

Ultrasonic velocities and viscosities of solutions of mixtures of KCl and NaCl at high concentrations were measured and hydration numbers calculated. Hydration decreased with molality.[542] With increasing concentration, there was either not enough water for all the ions or preferentially ion-pairing occurred. Some doubt was expressed whether "relative association" is a measure of hydration.

Ultrasonic absorption studies by the Carstensen method were made on $MnSO_4$ in water and in 25 wt % dioxane in

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water.[543] The data do not bear out the observations[544,545] that a relaxation peak existed at 35 Mc. This brought into question assignment of relaxation peaks to the steps in the association processes

$$M^{2+} + A^{2-} \overset{a}{\rightleftarrows} M^{2+}OH_2OH_2A^{2-} \overset{b}{\rightleftarrows} M^{2+}OH_2A^{2-} \overset{c}{\rightleftarrows} M^{2+}A^{2-} \qquad (89)$$

On theoretical grounds step a is not expected to yield a separate relaxation peak.[546] It was suggested[543] that the 200-Mc peak ought not to be assigned to step a but to step b. In the above mechanism only water molecules interposed between aquated ion-pair members are shown.

Ultrasonic absorption of aqueous solutions of (R_4N^+) halides, where R = ethyl, propyl, and butyl, showed a marked relaxation believed[547] to be associated with the special hydration properties of the alkylammonium cations.

In a study of the influence of ultrasound on electrode processes, the differences in discharge potential of the chloride anion in different alkali salts were correlated with the degrees of hydration of the cations.[548]

From the velocity of sound in aqueous solutions of NaCl, KCl, NaBr, KBr, NaI, KI, $MgCl_2$, $SrCl_2$, Na_2SO_4, and $MgSO_4$, the hydration numbers of the electrolytes up to 0.0625 M were calculated and compared with those obtained from compressibility measurements at higher concentrations.[549] The values obtained represented the primary hydration numbers and conform to the values determined by Robinson and Stokes[550] to fit experimental activity coefficients. Were some choice made for dividing the solvation numbers between the ions, the electrolyte solvation numbers could be resolved into those for individual ions.

The molar quantity of movement, MV, was defined by

$$MV = a + bM \qquad (90)$$

where M was the molecular weight and V the velocity of sound in the examined medium.[551] For solutions formulas were derived allowing for dissociation and hydration of solute molecules. Hydrations were estimated for different concentrations of NaCl, KCl, $NaNO_3$, KNO_3, urea, α-alanine, and glycine.

Ultrasonic absorption in aqueous solutions of the sulfates of Mg, Li, Na, and K for a given concentration was found[552] to decrease in the order $MgSO_4 > Li_2SO_4 > Na_2SO_4 > K_2SO_4$. In size Mg ion is between Li and Na; hence it was thought that the double charge of the Mg ion must be considered. These data seemed to confirm the idea that the larger the number of molecules bound by ions of large ionic radius, the lower the value of the ultrasonic absorption.

Measurements of the densities and sound velocities in liquid SO_2 of KI, MePyrI, Me_4NI, Et_4NI, Et_4NBr, Et_4NCl, Et_4NPic, Et_4NClO_4, $MePyrClO_4$, and Me_4NClO_4, where Pyr is pyridinium and Pic is picrate, were made.[553] The volume change when an electrolyte dissolved at zero concentration was much smaller for KI and Et_4NI in SO_2 than in water. This probably arose from the slight association of SO_2 in the liquid state and from its possible compressibility in the vicinity of the ionic charge. Also the SO_2 is larger than the water molecule and the SO_2 interaction with a large ion such as Me_4N^+ might be predominant.

The velocity of ultrasonic waves, densities, and adiabatic compressibilities of methanolic solutions of LiCl, NaCl, NaBr, NaI, and CsCl indicated[554] that the solvation numbers decreased in the order LiCl > NaCl > CsCl and were practically independent of the anion.

Ultrasonic interferometry and the quantitative determination of combined water gave complete saturation boundary values for the alkali halides, and for sulfates and nitrates of Na, K, Li, Ba, Cd, and Pb in aqueous solutions.[555] For alkali halides, a crystal lattice energy greater than the solvation energy ($\Delta H > 0$) indicated a complete solvation boundary concentration greater than the saturated concentration. $\Delta H < 0$ implied a complete solvation boundary concentration less than the saturated concentration.

If the hydration of cations is less than that of anions, the complete solvation boundary concentration is lower than the saturated concentration and *vice versa.* In general, the complete saturation boundary concentration relative to the saturated concentration depends on the hydration entropy of the ions of the electrolyte with the hydration capability of the cation a large factor in the complete solvation boundary values.

4. Significance

From Table XX, the solvation numbers of ions are dependent on the standard of reference chosen. This is to be expected when the solvation numbers of the same ions are compared for different standards of reference for solvation.

The solvation number of an ion depends on the solvent. Thus, the lithium ion has limiting solvation numbers at 25° of 3.6, 3.3, and 1.4, respectively, in water, methanol, and ethanol using as reference the solvation number of 2 for the nitrate ion. Similar numbers for the chloride ion are 2.3, 0.9, and 1.3 respectively. In general, the solvation numbers of cations for similar temperature and concentrations more closely correspond in water and methanol and differ comparatively more widely in ethanol. The solvation numbers of anions under similar conditions correspond more closely in methanol and ethanol and show comparatively wider variation in water.

The solvation number for an ion is not always the same as found by different investigators. Thus the limiting value of the solvation number of the ammonium ion in water from ref 500 is 1.1 or 3 depending on whether the reference standard for solvation numbers is taken as $K^+ = Cl^- = 3.2$ or $NO_3^- = 2$. In ref 526 the solvation number for the ion is given as zero.

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All investigators find by adiabatic compression, in opposition to other methods, a solvation number for the lithium ion which is low compared to those of the other alkali metal ions. Nmr indicated that structure breaking dominated structure making by this ion. If the dynamic solvation depicted[556] for the lithium ion is accepted and if this loosely constructed solvation permits some compressibility of the solvated ion, then the incompressibility of the solvated ion assumed in the adiabatic compressibility approach would account for this reverse in relative solvation number of the lithium as compared to the other alkali metal ions.

The adiabatic compressibility approach gives only the solvation for the primary solvation shells of ions.

I. EFFECTIVE VOLUME

1. Theoretical and Experimental

Darmois[557] showed that density measurements could be used to calculate primary solvation numbers. Consider a volume of solution, V, containing a total number of water molecules, n_1, of which n are attached to each of the n_2 salt molecules present in the total volume of solution as primary hydration water. If v_1 is the volume of one free water molecule, then $(n_1 - n_2n)v_1$ is the volume of free water in the volume V. Let V_s be the Stokes volume of one of the hydrated ions in the volume V_1; then the primary hydration number, n, can be calculated from the equation

$$(n_1 - n_2n)v_1 + n_2V_2 = V \tag{91}$$

However, it has been shown that this method has a basic weakness in that it depends upon the Stokes volume which is often too small, thereby yielding hydration numbers that may also be too small.[558]

Conway and Bockris[558,559] suggest that a better method would be to express the Stokes volume in terms of the crystallographic volumes of the ions, v_i, and of the compressed water molecules, nv_1^{h}. Therefore

$$V = (nv_1^{\mathrm{h}} + v_i)n_2 + (n_1 - n_2n)v_1 \tag{92}$$

Introducing the apparent molal volume, ϕ, and solving for n, one obtains

$$n = \frac{\phi - v_i}{v_1^{\mathrm{h}} - v_1} \tag{93}$$

The $v_1^{\mathrm{h}} - v_1$ term was evaluated from data for the pressure created by the Coulombic ionic field in a surrounding dielectric at a mean distance, $V_1 + V_{\mathrm{w}}$, from the center of the ion[560] and from data for the compressibility of water at these pressures.[561] Using known literature values for the apparent molal volume,[562–564] the primary hydration numbers for the following ions were obtained: Li^+ (n = 2.5), Na^+ (n = 4.8), K^+ (n = 1.0), F^- (n = 4.3), and Cl^- (n = 0).

Goto[565] has determined the effective volumes, the apparent volumes, and the magnitudes of electrostriction for a number of 1:1 electrolytes in aqueous solution from an analysis of the densities of solutions at different concentrations. From these data the number of molecules of water of hydration associated with the various electrolytes was obtained. The method of Goto may be outlined as follows. The reciprocal of the density (d_{m}) of a solution containing m grams of solute in 100 g of the solution corresponds to the volume, V_{m}, of 1 g of the solution. Consequently, the volume, V_{c}, of a solution containing 100 g of water and c grams of solute may be written as

$$V_{\mathrm{c}} = c\bar{v} + \frac{100}{d_0} - V_{\mathrm{c}}^{\mathrm{e}} \tag{94}$$

where $\bar{v}$ is the effective specific volume of salt in the solution, d_0 is the density of pure water, $V_{\mathrm{c}}^{\mathrm{e}}$ is the volume of water decreased by electrostriction, and c is given by

$$c = \frac{100m}{100 - m} \tag{95}$$

If the concentration of the solute, c, is changed from c_i to c_j, then

$$\bar{v}_{i,j} = \bar{v} - \frac{V_{\mathrm{ci}}^{\mathrm{e}} - V_{\mathrm{cj}}^{\mathrm{e}}}{C_i - C_j} = \bar{v} - \frac{\mathrm{d}V^{\mathrm{e}}}{\mathrm{d}c} \tag{96}$$

where $\bar{v}_{i,j}$ is the apparent specific volume of the salt for a given concentration range. If $\mathrm{d}V^{\mathrm{e}}/\mathrm{d}c = 0$ or if $V_{\mathrm{ci}}^{\mathrm{e}}$ becomes equal to $V_{\mathrm{cj}}^{\mathrm{e}}$ as the concentration is increased, then $\bar{v}_{i,j}$ will correspond to the effective specific volume of the salt in solution since all the solvent water will be attracted by ions at a high concentration. Under such conditions, the volume of water (100 g) may approach a constant $(100/d_0 - V^{\mathrm{e}}_{\mathrm{max}})$ with an increase in the concentration of the solute. The correlation between V_{c} and the salt concentration was found to be represented empirically by

$$V_{\mathrm{c}} = c\bar{v} + (100/d_0) - (1 - r^c)V^{\mathrm{e}}_{\mathrm{max}} \tag{97}$$

The parameters, $V^{\mathrm{e}}_{\mathrm{max}}$, r, and $\bar{v}$ were determined by the method of least squares. Also the difference between $\bar{v}_{i,j}$ at infinite dilution or the apparent specific volume, $\bar{v}_0$, of a salt, and its effective specific volume, $\bar{v}$, corresponds to the magnitude of electrostriction, v^{e}, per 1 g of salt at infinite dilution or

$$v^{\mathrm{e}} = \bar{v} - \bar{v}_0 = kV^{\mathrm{e}}_{\mathrm{max}} \tag{98}$$

Since the volume of the solution does not increase linearly with concentration as the result of the electrostriction of the solvent, two curves were drawn for the volume of the solution (V_{c}) and of the solvent (V_{s}) under conditions: $\mathrm{d}V_{\mathrm{c}}/\mathrm{d}c > 0$, $\mathrm{d}^2V_{\mathrm{c}}/\mathrm{d}c^2 > 0$ and $\mathrm{d}V_{\mathrm{s}}/\mathrm{d}c < 0$, $\mathrm{d}^2V_{\mathrm{s}}/\mathrm{d}c^2 > 0$. These curves were analyzed using eq 97 for solutions of 1:1 electrolytes from which it was determined that the effective specific volumes, $\bar{v}$, of a salt in aqueous solution and the maximum volumes, $V^{\mathrm{e}}_{\mathrm{max}}$, of water decreased by the electrostriction. Then the apparent specific volumes, $\bar{v}_0$, and the magnitudes of the electrostriction, v^{e}, were calculated from eq 98. It can then

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be shown that the number of molecules of water of hydration per molecule of solute is given by the expression

$$N = \frac{(100v^{e}/V^{e}_{\max})(\text{molecular weight of solute})}{18} \tag{99}$$

The values obtained are given in Table XXI. The large values for the hydration numbers were discussed in terms of the probability of clathrates around the ions.

Table XXI[a]

Salt	N^b	*Salt*	N^b
LiCl	30	KI	47
LiBr	51	RbCl	49
LiI	66	RbBr	38
NaCl	22	RbI	28
NaBr	37	CsCl	45
NaI	42	CsBr	87
KCl	34	CsI	96
KBr	46		

[a] Values obtained at 20°. [b] Moles of H_2O/mole of solute.

The previous discussion has shown that the volume contraction produced by the interaction between ions and water molecules can be used as a measure of the magnitude of hydration. The volume contraction calculated from compressibility data has been shown to be proportional to the amount of hydration water, the proportionality constant being independent of the temperature and the nature of the electrolyte.[566–568]

Tamura and Sasaki[569] have developed a method based upon the empirical equation of Tait,[570] which gives the compressibility of water under pressure, from which a quantity is obtained which the authors proposed as a common parameter of hydration.

The Tait equation may be written as

$$\beta^{(p)}V_1^{(p)} \equiv (\partial V_1^{(p)}/\partial P)_T = 0.4343C/(B + P) \tag{100}$$

or in the integrated form

$$V_1^{(p_0)} - V_1^{(p)} = C \log [(B + P)/(B + P_0)] \tag{101}$$

where β is the isothermal compressibility, V is the molar volume of water, B and C are constants dependent upon the temperature and nature of the liquid, P is the external pressure, and P_0 is the standard pressure of 1 bar. The dissolution of an electrolyte in water produces a state of electrostriction[571] which causes water to behave like a substance placed under a constant effective pressure which is greater than atmospheric pressure by an amount P_e.[572] Equation 100 can now be written as

$$V_1^{(p)} - \Phi_1^{(p)} = C \log [(B + P + P_e)/(B + P_0)] \tag{102}$$

where $\Phi_1^{(p)}$ is the volume occupied by 1 mol of water in an electrolyte solution under an external pressure P which is, therefore, the molar volume of pure water under the pressure $(P + P_e)$. A solution containing n mol of water and 1 mol of solute has the volume

$$V^{(p)} = n\Phi_1^{(p)} + \Phi_2^{(p)} \tag{103}$$

where $\Phi_2^{(p)}$ is the contribution to the volume of the solution made by 1 mol of solute. Therefore, if $P = P_0$

$$V^{(p)} = nV_1^{(p_0)} - nC \log [(B + P_0 + P_e)/(B + P_0)] + \Phi_2^{(p_0)} \tag{104}$$

or

$$\beta(V)^{p} = 0.4343Cn/(B + P + P_e) - (\partial\Phi_2^{(p)}/\partial P)_T \tag{105}$$

Assuming the last term to be negligible at moderate pressures and concentrations,[573] *one can obtain the expression*

$$\Phi_2^{(p_0)} = V^{(p_0)} - n_1V_1^{(p_0)} + nC \log \; n\beta^{(p_0)}V_1^{(p_0)}/\beta^{(p_0)}V^{(p_0)} \tag{106}$$

Equation 106 was used to calculate $\Phi_2^{(p_0)}$ from the isothermal compressibilities, obtained by sound velocity measurement,[573] and densities of both pure water and the solutions. Values of $\Phi_2^{(p_0)}$ were obtained for a number of electrolytes and compared with the molar volumes of the same electrolytes in the supercooled liquid state (the molar volume of a molten electrolyte at a high temperature was calculated and extrapolated to the temperature corresponding to those at which $\Phi_2^{(p_0)}$ were calculated). Satisfactory agreement was found between the two values obtained for each electrolyte which supports the view that the solute in a solution behaves as a supercooled liquid with respect to its contribution to the volume of the solution.

In obtaining a parameter of hydration, a method was adopted based on the incompressible hydration shell model.[574,575] *Assuming that the hydration shells together with* the hydrated ions are incompressible, then the volume of water, V_h, bound to 1 mol of solute in solution, reduced to atmospheric pressure, P_0, is

$$V_h = (n\beta^{(p_0)}V_1^{(p_0)} - \beta^{(p_0)}V^{(p_0)})/\beta_1^{(p_0)} \tag{107}$$

$$V_h = -K_2/\beta_1^{(p_0)} \tag{108}$$

where K_2 is the apparent molal compressibility of the solute. The values of V_h may be determined from compressibility and density data. The average hydration number of water molecules for a pair of solutes is then defined by

$$h = V_h/V_1^{(p_0)} \tag{109}$$

Values of h obtained for a number of electrolytes are shown in Table XXII.

In the development of an equation for the molar volume of ions in aqueous solution which includes all types of ions to temperatures up to 200°, Glueckauf[576] calculated the number of water molecules in a number of layers around the ions. The apparent molar volume ϕ of ions in water at infinite dilution was expressed in terms of the intrinsic volume, V^0, of the ion from which was subtracted the volume change arising as the result of forces exerted by the ion on the water dipoles.

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Table XXII

Salt	*Hydration no., h*	*Temp, °C*
LiCl	4.24	25
$LiNO_3$	2.98	25
NaCl	5.96	20
	4.98	25
NaBr	4.82	20
NaI	3.37	20
NaOH	8.40	25
KCl	5.17	20
	4.44	25
KBr	3.97	20
KI	2.92	20
NH_4Cl	1.50	25
$MgCl_2$	11.50	20
	10.40	25
$Mg(NO_3)_2$	8.38	25
$CaCl_2$	11.30	20
$Ca(NO_3)_2$	7.60	25
$BaCl_2$	12.60	20
	11.40	30
	11.10	40
Na_2CO_3	19.10	20
	15.70	25
Na_2SO_4	18.20	20
K_2SO_4	14.40	25
$(NH_4)_2SO_4$	9.34	25
$MgSO_4$	14.70	25
$CuSO_4$	13.20	25

Assuming that water at its normal density surrounds a spherical ion, then, because of the open structure of water, there will be a certain amount of dead space that has to be included in the intrinsic volume. The intrinsic volume can then be expressed by

$$V^0 = (4/3)\pi(r_0 + a)^3N \tag{110}$$

where

$$a = (3v_w/4\pi N)^{1/3} - r_w \tag{111}$$

where r_0 is the radius of the ion, r_w is the radius of the water molecule (1.38 Å)$_1$, v_w is the molar volume of water at a given temperature.[577] If one envisions each ion originally surrounded by water molecules in such a way that the density is everywhere that of water, then the first layer will have its center at $r_1 = r_0 + r_w = \bar{r}$, and for subsequent layers it is assumed that the distance of each layer increases by 1.76 Å. It is noted that this distance is only correct for ions equal in size to the water molecule. However, this difference is not important at these relatively large distances from the ion. The number of water molecules χ_n in the nth layer surrounding an ion was calculated in the following manner. Each sphere of radius r_n contains approximately $(1/2)\chi_n$ water molecules with the center at r_n plus all the water molecules at $r < r_n$, plus the intrinsic volume of the ion. Therefore

$$\chi_1 = (8/3)(\pi/v_w)r_1^3 - 2(V^0/v_w) \tag{112}$$

or

$$\chi_n = (8/3)(\pi/v_w)r_n^3 - 2(V^0/v_w) - 2\sum_{a=1}^{a=n-1}\chi_a \tag{113}$$

The number of water molecules in the nth layer was calculated for the ions shown in Table XXIII.

Table XXIII

Number of Water Molecules in the nth Layer at 25° in the Uncompressed State

	Layers			
Ion	*n = 1*	*n = 2*	*n = 3*	*n = 4*
I^-	7.3	22	35	60
Cs^+	5.1	18	30	53
K^+	3.8	16	27	48
Li^+	2.0	11	22	41

Benson and Copeland[578] have shown that the Mukerjee[579,580] hypothesis of correlating partial molar volumes of ions with the continuum model of Born can be understood in terms of an isomorphic replacement of water molecules in a simple cubic lattice by ions whose sizes range from smaller to not too much larger than water. From the arguments developed optimum values for coordination numbers of 6 to 8 were calculated for ions of radius between 1 and 2 Å.[578]

Partial molal volume data were used by Padova[581] to determine the solvation numbers of the lanthanides in aqueous solution. The solvation numbers were obtained with the equation[582]

$$\bar{V}_h = \bar{V}_2^0 + n^0\bar{V}^0 \tag{114}$$

where $\bar{V}_h$ is the molar volume of the hydrated ion, $\bar{V}_2^0$ the partial molal volume at infinite dilution of the lanthanide salts in water, $\bar{V}^0$ the partial molal volume of water at infinite dilution, and n^0 the solvation number. The values of $\bar{V}_h$ were obtained from the relationship between the B coefficient of the Jones–Dole equation[583] and $\bar{V}_h$: $\bar{V}_h = B/2.5$[584] The values for B and $\bar{V}_2^0$ were taken from the literature.[585,586] Values for the ionic solvation numbers were then obtained by using values for the chloride ion of $n^0 = 1$ and $\bar{V}_2^0 = 18.60$.[587] The following solvation number values were obtained for the lanthanides: La^{3+} (8.5), Pr^{3+} (9.5), Nd^{3+} (9), Sm^{3+} (9.5), Tb^{3+} (10), Dy^{3+} (11), Ho^{3+} (11), and Er^{3+} (11).

The apparent molar volumes of HCl, HNO_3, H_2SO_4, KOH, and NaOH have been determined at 15°.[588] Assuming that the hydration number of H^+ is 1 and that of OH^- is 0, the following hydration numbers were determined from the data: SO_4^{2-} (2), Cl^- (3), NO_3^- (3), K^+ (4), and Na^+ (10).

Solvation numbers have been calculated from the apparent molar volumes of electrolytes in sulfuric acid.[589,590] The

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Table XXIV

Solvation Numbers (*n*) of Ions in Sulfuric Acid

Ion	*n*	*s*
Ba^{2+}	6	6.5
Na^+	3	3.0
Li^+	3	2.3
K^+	2	2.1
NH_4^+	1	1.2
Rb^+	0.7	

values obtained (n) are shown in Table XXIV based upon a value of 3 for the sodium ion.[591] The relationship between osmotic coefficient and apparent molar volume was also used to obtain the solvation numbers of ions (s) in sulfuric acid as shown in Table XXIV.[591]

If one treats the solutions as if containing a single electrolyte species of molality, m, the variation of the osmotic coefficient with electrolyte concentration may be expressed as

$$\phi = 1 + \phi_{el} + b\sum m \tag{115}$$

where ϕ_{el} is the electrostatic interionic contribution to the osmotic coefficient, Σm the total concentration of ionic species, and b the osmotic coefficient parameter which is related to the solvation number (s) of the electrolyte by

$$b = [(r + s)^2/40.8] - (r/20.4) \tag{116}$$

In eq 116, r is the ratio of the apparent molar volume of the electrolyte to the molar volume of the solute, 54 cc, and s is the solvation number of the electrolyte.[591] Values of b were determined from osmotic coefficients using freezing point data.[592] A comparison has been made of the solvation numbers derived from cryoscopic and density measurements.[593]

J. DIELECTRIC PROPERTIES

The molar dielectric depression observed in aqueous solutions of ions has been discussed assuming that the first shell of water molecules is dielectrically saturated with respect to positive ions and unsaturated in the case of negative ions.[594] It was found from the results of dielectric constant measurements made at centimeter wavelengths and extrapolated to zero frequency that the dielectric constant depends on the salt concentration in the following manner

$$E_s = E_{H_2O} - \delta_c \tag{117}$$

where E_s is the dielectric constant of the electrolyte solution, E_{H_2O} the dielectric constant of pure water, c the electrolyte concentration, and δ given by

$$\delta = 1.5\left[\frac{V_2(E_{H_2O} - E_{\infty,ions})}{1000} + V_{H_2O}\frac{(E_{H_2O} - E_{\infty,H_2O})}{1000}n\right] \tag{118}$$

where values of $E_{\infty,ions}$ and E_{∞,H_2O} are taken as 2 and 5.5, respectively, V_2 and V_{H_2O} are the molar volumes of the solute and water, respectively, and n is the primary hydration number. Equations 117 and 118 were used to calculate the primary hydration numbers for a number of salts as shown in Table XXV.[595]

Table XXV

Primary Hydration Numbers of Salts from Dielectric Constant Measurements

Salt	*n*	*Salt*	*n*
NaF	4 ± 1	KCl	5 ± 1
NaCl	6 ± 1	RbCl	4 ± 1
NaBr	6 ± 1	NH_4Cl	4 ± 1
NaI	6 ± 1	KF	5 ± 1
LiCl	6 ± 1		

To determine primary hydration numbers for individual ions, one must assume the relative contributions of the two ions in a single case. The parameter δ can then be written as $\delta = (\delta^+ + \delta^-)/2$. Using NaCl as a reference and taking into consideration that a small amount of water outside the first hydration sphere is also dielectrically saturated, the following minimum hydration numbers were obtained (Table XXVI).[594]

Table XXVI

Minimum Hydration Numbers of Positive Ions

Ion	*n*	*Ion*	*n*
H^+	10	Rb^+	4
Li^+	6	Mg^{2+}	14
Na^+	4	Ba^{2+}	14
K^+	4	La^{3+}	22

Glueckauf[596] states that the assumption that positive ions are surrounded by a dielectrically saturated first shell of water molecules, while negative ions have their first shell of water molecules completely unsaturated, is incapable of giving a quantitative description of the decrease in dielectric constant with added electrolyte and that, in fact, the fields in the neighborhood of all monovalent ions with the exception of H^+ are such that the first shell is far from saturated. Glueckauf[596] determined the dielectric constants of aqueous electrolyte solutions by integrating over the spatial distribution of the local dielectric constants in the manner appropriate for disperse systems. Using the dielectric constant change of the water molecules as a rough measure of their immobilization, a mean hydration number was determined from the equation

$$h = \sum_p \bar{n}_p\left(1 - \frac{D_{wp} - n^2}{D_0 - n^2}\right) \tag{119}$$

where $\bar{n}_p$ is the number of water molecules that can be fitted into the pth shell, D_{wp} is the mean dielectric constant of the water molecules in that layer, and D_0 is the dielectric constant of water at zero field strength. A rough estimate of the mean hydration number, h, from D_{wi}, the value of D for first layer water molecules, is given in Table XXVII.[596]

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Table XXVII

The Hydration Number, *h*, Determined from D_{wi}

Ion	*h*	*Ion*	*h*
H^+	4	Cs^+	12
Li^+	6	F^-	10
Na^+	8	Cl^-	13
K^+	10	I^-	16

K. X-RAY

There have been a number of attempts to use X-rays to study the structure of ionic solutions. Stewart studied the variation in the structure of water in ionic solutions using liquid diffraction curves of water in these solutions.[597]

Prinns[598] obtained qualitative evidence of structrue in aqueous solutions of $Th(NO_3)_4$, $UO_2(NO_3)_2$, $AgNO_3$, $Pb(NO_3)_2$, $Ba(NO_3)_2$, LiI, RbBr, and LiBr. It was shown that the X-ray diffraction patterns could be associated with the different stuctural elements in the solution. The intensity was assumed to be the result of three distributions: the scattering due to the ions, the scattering due to the water structure, and the scattering due to ion–water structure. If the distribution function characteristic of each of these terms were known, one would then be able to obtain information about the hydration number and interionic distance as a function of concentration. Other ionic solutions have been studied for which radial distribution functions of NaOH, HCl, and H_3PO_4 have been determined; however, peak resolution in the distribution functions was not sufficient to permit the attainment of direct quantitative information.[599–602]

Brady and Krause performed X-ray diffraction studies on concentrated KOH and KCl solutions and from the radial distribution functions obtained, hydration numbers could be calculated.[603] The distribution functions of two KOH solutions were found to contain primary peaks with maxima at about 2.87 Å for a 18.8% solution and 2.92 Å for the 11.4% solution. Beyond this primary peak the curves indicate that there is a region of decreased electron density followed by a peak at 4.75 Å. The identification of the peaks was made from information pertaining to the structure of water and the ionic radii of the species involved. The 4.75-Å peak corresponds to the second nearest neighbor distance in water. Water with its tetrahedral structure has its second nearest neighbor distance as the length of the tetrahedral edge. The calculated value of this length based on a nearest neighbor distance of 2.92 Å is 4.75 Å, in good agreement with the observed value. The ionic radii of K^+ and OH^- are both 1.33 Å, and H_2O has an effective radius of 1.38 Å. The nearest neighbor peak for liquid H_2O at 30° has its maximum at 2.94 Å. Since the radius of H_2O and the radii of the ions are very similar, one would expect only a slight change in peak position in KOH solution. The primary peaks exhibited only one maximum, and it was concluded that the primary peak in the KOH distribution functions includes nearest neighbor H_2O molecules, K^+–H_2O neighbors, and OH^-–H_2O neighbors. There was also evidence that some of the nearest neighbors are constantly changing position with other molecules in solution. From an analysis of the peak area in terms of the number of molecules around OH^-, the number of molecules around K^+, and the number of nearest neighbor H_2O molecules around any other H_2O molecule, a hydration number of 4 was obtained for the K^+ ion. A subsequent X-ray investigation of aqueous solutions containing K^+, Li^+, OH^-, and Cl^- gave hydration numbers of 4, 4, 6, and 8, respectively.[604] Coordination numbers have also been determined for Li^+, Na^+, K^+, OH^-, and Cl^- from the X-ray analysis of aqueous solutions of these ions by Skryshevskii.[605] Hydration numbers for K^+ and Na^+ of 4 and 5.5, respectively, have been determined from the X-ray analysis of sulfate solutions.[606] The X-ray diffraction of water and a number of electrolyte solutions has been measured from which radial distribution functions were obtained.[607] Evidence was obtained that suggests that the K^+ and Ca^{2+} ions are surrounded by six water molecules coordinated octahedrally. X-Ray diffraction studies of aqueous solutions of magnesium tetrafluoroborate indicate that the number of water molecules in the first hydration shell around the Mg^{2+} ion is 6 and that in dilute solutions the number of water molecules in the second hydration shell is 10–11.[608] Aqueous solutions of $ZnBr_2$ and $ZnCl_2$ have been studied using X-ray techniques and evidence has been obtained for a coordination number of 4 for Zn^{2+}.[609,610]

L. NUCLEAR MAGNETIC RESONANCE

Solvation numbers have been determined for a number of ions by various nuclear magnetic resonance (nmr) techniques.[611] In an electrolyte solution, the solvent molecules can exist in several environments. These environments may be arbitrarily divided into bulk solvent regions, where solvent molecules are effectively out of range of ionic influence, secondary solvation regions, and primary solvation regions.[612] If exchange of molecules between all of these environments were very slow, then a number of peaks would be expected in the nmr spectrum of the solvent nuclei corresponding to the different interactions. Generally, the exchange of solvent molecules between the different environments is very rapid; consequently, the separate resonance signals expected for each environment are time averaged to a single peak whose shift from the pure solvent resonance peak reflects the mean effect of the different environments. However, certain experimental techniques have been developed that permit the observation of bulk and bound solvent molecules.

Primary and secondary solvation numbers have been determined for a number of ions by various nmr techniques. The most direct approach involves the observation and peak

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area determination of resonance peaks associated with the bulk solvent and with the bound solvent (*i.e.*, solvent molecules coordinated with the ions). The initial study of this type[613] was that in which the $H_2{}^{17}O$ nmr spectrum of several aqueous solutions revealed peaks attributed to bulk and bound solvent. The ^{17}O nucleus was used as a "probe" due to the magnitude of the chemical shifts which had been observed for this nucleus.[614] The first ions chosen for study were Al^{3+}, Be^{2+}, Ga^{3+}, and $(NH_3)_5Co(H_2O)^{3+}$, the last one being chosen because the number of water molecules attached to the Co^{3+} ion is known[615] and because of the long exchange time of the bound water with bulk water. The ^{17}O nmr spectra of aqueous solutions of these ions showed only a single resonance peak for water; however, upon the addition of a small amount of Co^{2+} to the system, separate peaks appeared that were associated with bulk solvent molecules and those water molecules bound by the ions.[613] Previous work[616,617] had shown that paramagnetic ions produce large shifts in the resonance absorption of other nuclei.[616,617] The addition of Co^{2+} to the solutions enabled bulk and bound solvents molecules to be observed because a great many more bulk water molecules come into contact with Co^{2+} ions than the water molecules bound to the Al^{3+}, Be^{2+}, Ga^{3+}, or $(NH_3)_5Co(H_2O)^{3+}$ ions; consequently, the bulk water resonance signal undergoes a large shift while no significant contribution is made to the shift of the bound molecules.

Since it is possible to separate the ^{17}O nmr signals of bound and bulk solvent water, the number of water molecules held in the primary sphere can be calculated in one of two ways: by comparing the areas under the two ^{17}O resonance peaks or by measuring the shift of the resonance peak produced by the paramagnetic ion in the presence and absence of the diamagnetic ion.

Although the precision of measurement (unfavorable signal-to-noise ratio) was not sufficiently high for Jackson, Lemons, and Taube[613] to determine the number of water molecules associated with Al^{3+}, Be^{2+}, or Ga^{3+}, Connick and Fiat[618] were able to determine the coordination of Al^{3+} and Be^{2+} with the peak area comparison method by increasing the signal-to-noise ratio using water of greater ^{17}O enrichment and the sideband detection technique. Solutions of $AlCl_3$ and $BeCl_2$ to which Co^{2+} ions had been added gave an average solvation number of 5.9 and 4.2 for Al^{3+} and Be^{2+}, respectively.

Alei and Jackson[619] have determined the solvation numbers of Al^{3+}, Be^{2+}, and Cr^{3+} ions using the chemical shift method.[613] In an aqueous solution of a paramagnetic ion in which there is a rapid exchange of water molecules between the first coordination sphere of the ion and the bulk of the solvent, a single $H_2{}^{17}O$ nmr signal is observed. This resonance signal is shifted from its normal position in pure water by an amount dependent on the ratio of the concentration of the paramagnetic ion to the total labile water present. The addition of a second ion for which the water in the first coordination sphere is nonlabile causes a decrease in the amount of water available to interact with the paramagnetic ion and, consequently, a change in the labile $H_2{}^{17}O$ resonance position is observed. From this change the number of moles of labile water in the solution containing the diamagnetic and paramagnetic ions can be calculated. The difference between the known total number of moles of water and the number of molecules of labile water divided by the number of moles of the diamagnetic ion gives the solvation number of the diamagnetic ion. Using Dy(III) as the paramagnetic ion whose effect on water was known,[620] the solvation numbers of 5.9 and 3.8 were obtained for the Al^{3+} and Be^{2+} ions, respectively.

The chemical shift method of determining solvation numbers may also be applied to paramagnetic ions if the magnetic influence of the paramagnetic ion does not extend beyond the first solvation sphere.[619] However, with modification this method was also applied to the Cr(III) ion whose magnetic influence does extend beyond the first solvation sphere and produces a shift in the labile $H_2{}^{17}O$ resonance. A value of 6.8 was obtained for the solvation number of Cr(III).[621] This value is significantly greater than the value of 6 determined by the isotope dilution method.[622] This discrepancy and the validity of the assumptions made in acquiring the value, 6.8, were discussed by the authors.

The chemical shift method has been used to determine the hydration numbers of certain organometallic cations.[623,624] The hydration number of $(CH_3)_3Pt^+$ was found to be 3. In solutions containing $(NH_3)_2Pt^+$ ions, however, bulk and bound water resonance signals were observed from which a hydration number of 2 was obtained for the cation.

Cation hydration numbers in hydrate melts have also been obtained for melts of calcium nitrate tetrahydrate with anhydrous potassium nitrate, tetramethylammonium nitrate, and magnesium nitrate using the chemical shift method.[625] The proton chemical shifts of water indicate that in melts with nitrates of univalent cations the Ca^{2+} ion is selectively hydrated. In melts with $Mg(NO_3)_2$, the Mg^{2+} ion was found to be selectively hydrated at the expense of the Ca^{2+} ion.

Solvation numbers of 3.8 ± 0.2[626] and 6.28 ± 0.26[627] have been obtained for the V(IV) ion and the Ga(III) ion, respectively, by the chemical shift method.

The hydration numbers for several electrolytes have been determined from temperature effects on the proton shift of water.[628–633] The proton shift of water is strongly dependent upon temperature,[634] being an average of the bonded and non-

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bonded environments of the proton. Water vapor having few hydrogen bonds is characterized by a high field shift. The chemical shift of pure water was measured relative to gaseous ethane over the temperature range of 5–95°.[628] Ethane was used as the reference because its shift is independent of temperature. Over the temperature range studied, the proton chemical shift was found to be a linear function of temperature as described by the equation

$$\delta_{H_2O} = 0.00956t - 4.38 \text{ ppm} \qquad (120)$$

where t is the temperature in degrees centigrade.

In an aqueous electrolyte solution, a single resonance signal is observed for water protons that is the weighted average of the different environments experienced by the protons. Any given proton residing in the normal water structure has a shift δ_N that is identical with the shift, δ_{H_2O}, of pure water at the temperature of the observation. Protons of water molecules involved in the solvation of an ion have a resonance signal that is shifted relative to that of pure water. This solvation shift, δ_S, depends upon both the cation and anion. Since the average time a proton resides in any environment is proportional to its instantaneous mole fraction, the proton shift observed for an aqueous solution can be written as

$$\delta_{H_2O} = X_N\delta_N + X_S\delta_S \qquad (121)$$

where X_N and X_S are the mole fractions of protons in the normal water and hydrated form. This assumes that water molecules beyond the first solvation sphere are unaffected by the ions. If h represents the total effective solvation number (*i.e.*, moles of solvated water per stoichiometric moles of salt) and m represents the stoichiometric molality, eq 121 becomes

$$h = (55.55/m)[(\delta_{H_2O} - \delta_N)/(\delta_S - \delta_N)] \qquad (122)$$

Equation 122 also predicts a linear relationship between shift and molality if h and δ_S remain independent of concentration and indicates that at some temperature, $\delta_{H_2O} = \delta_N$. Obviously, at this temperature $\delta_S = \delta_N$. Assuming that the shift of a proton in the solvated environment does not vary with temperature, the effective solvation number of the salt may be calculated from this equation. Substitution of the experimentally determined values of the parameters into eq 122 gives a total effective hydration number for the electrolyte in question. Effective hydration numbers of a number of electrolytes determined by the method are shown in Table XXVIII.

Two explanations may be given for the high values of h obtained for the Mg^{2+}, Ca^{2+}, and Al^{3+} salts. The first is that the anions have a definite hydration number which contributes to the total effective hydration number. The second explanation considers a contribution of secondary hydration layer to the total hydration.

A study of the ^{7}Li nmr of aqueous lithium halide solutions revealed a downfield chemical shift in resonance position with an increase in concentration.[635] Plots of chemical shift *vs.* mole fraction of salt were linear up to a mole fraction of 0.3. The shifts were also apparently temperature independent. The observed shifts were interpreted in terms of a progressive polarization of the lithium ion by the close approach of an increasing proportion of anions. The data suggest a solution model of a relatively random mixture of ions and molecules with no lasting interaction between them; furthermore, the data are not compatible with the concept of a tightly bound hydration shell or of a tightly bound ion pair. The average number of sites available for competition around the lithium ion was calculated from $\delta = \delta^0 X m$, where δ is the observed chemical, δ^0 is the limiting shift corresponding to the pure halide, X is the number of sites, and m is the mole fraction of salt. From a plot of δ/δ^0 *vs.* m, a value of $X = 2$ was obtained for values of $m < 0.3$. It was suggested that this value of X does not so much represent the classical hydration number as the average number of sites accessible to halide substitution. The number might also represent the effectiveness of the water molecules to exclude anions from the cation.

Table XXVIII

Total Effect Hydration Numbers of Electrolytes Determined from Temperature Dependence of Proton Shifts

Compd	*h*	*Ref*	*Compd*	*h*	*Ref*
HCl	3.4	632	KCl	4.6	630
HNO_3	2.8	629	KI	4.1	629
$HClO_4$	2.6	632	RbOH	5.2	629
LiCl	3.2	629, 630	RbCl	4.0	630
LiBr	4.4	629	CsCl	3.9	630
NaOH	2.9	629	$MgCl_2$	8.2	630
NaCl	4.5	630	$Mg(ClO_4)_2$	8.0	629
NaBr	4.4	630	$CaCl_2$	9.5	629, 630
$NaNO_3$	3.3	629	$Ca(NO_3)_2$	7.8	629
$NaClO_4$	3.0	630, 632	$Ca(ClO_4)_2$	8.6	629
Na *p*-Ts[a]	2.8	630	$Al(NO_3)_3$	13.4	632
KF	3.8	629			

[a] Sodium *p*-toluenesulfonate.

Swinehart and Taube[636] determined the solvation number of the magnesium ion in methanol by an nmr technique based upon the ability to detect bulk and bound methanol molecules. Proton nmr spectra of solutions composed of 1 mol of $Mg(ClO_4)_2$:17.1 mol of CH_3OH:1.4 mol of H_2O and 1 mol of $Mg(ClO_4)_2$:17.1 mol of CH_3OH:3.8 mol of H_2O taken at −75° showed separated hydroxyl proton resonance peaks for methanol in the bound and bulk state. A solvation number of 5.7 ± 0.2 was determined for the magnesium ion from measurements of the resonance peak area associated with the bulk and bound hydroxyl protons of methanol and with the water proton. The deviation from a value of 6 for the solvation number was attributed to association of magnesium with the perchlorate ion. The separation of the absorption signals for the bulk and bound solvent environments was feasible because of the low temperature employed in recording the spectra. At −75° the frequency of exchange of nuclei between the two environments was small compared to the frequency difference between the chemical shifts. At −85° it was observed that a decrease in the amount of solvation water relative to the amount of solvation methanol occurred at this temperature, indicating reequilibration of water between the solvated cation and solvent.

A more extensive study of the $Mg(ClO_4)_2$–methanol system has been made by Nakamura and Meiboom.[637] At low temperature the OH protons of the methanol molecules bound to the Mg^{2+} ion gave a resonance peak well separated from the bulk OH peak. The symmetry of the OH quadruplet of

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methanol molecules in the solvation shell suggests a regular octahedral configuration in the first solvation shell under the conditions studied. The exchange of the OH protons of the methanol molecules in the solvation shell with bulk solvent and for exchange within the solvent complex is very slow as indicated by the well-defined structure of the quadruplet. The solvation number of the magnesium ion in anhydrous methanol was determined from the molar ratio of $Mg(ClO_4)_2$ and methanol in the solution and the ratio of the area under each resonance signal. The solvation number obtained in this manner was 6. No appreciable "close" ion association was indicated by the data since the solvation number determined remained constant even at high concentration of $Mg(ClO_4)_2$ and at very low temperature. Penetration of the perchlorate ion into the first solvation shell of the Mg^{2+} ion would have caused a decrease in the calculated solvation number.

The addition of a small amount of $Cu(ClO_4)_2$ to the $Mg(ClO_4)_2$–CH_3OH system was found to broaden the bulk OH and CH_3 proton resonance signals while the proton signals of solvation shell methanol molecules are only slightly affected. This technique[613] provides an excellent method for determining whether the exchange of protons of the solvation shell is due to protons only or to whole molecules. It was found that the CH_3 and OH proton resonance signals of the solvation shell molecules broaden and disappear at the same time as the temperature is increased, demonstrating that the whole molecule is exchanging in the solution.

Other nmr studies of the Mg^{2+} ion in aqueous acetone solution[638-640] and in methanolic acetone solution[640] indicate that the solvation number for this cation is 6. This value was obtained by the bulk-bound signal area ratio method. Direct evidence of anion shifts in the hydroxyl proton resonance spectrum of methanol solutions of magnesium perchlorate has been obtained.[641] The solvation number of the Mg^{2+} ion in liquid ammonia has been determined to be 5.[642]

A solvation number of 6 has been obtained for Co^{2+} in anhydrous methanol,[643] water,[644] *N*,*N*-dimethylformamide,[645] and acetonitrile,[646] using the bulk-bound signal area ratio method. In these solutions no consistent trend of the solvation number was discernible with either temperature or solution composition.

A solvation number of 6 has been obtained for Al^{3+} in dimethylformamide,[647] anhydrous dimethyl sulfoxide,[648] aqueous dimethyl sulfoxide,[649] and water[650-655] by the bulk-bound signal area ratio method. It is also of interest to note that separate resonance peaks corresponding to differently hydrated aluminum ions have been observed in the spectrum of aqueous acetonitrile solutions of $Al(ClO_4)_3$.[656] Solvation numbers of 4 for Be^{2+} in dimethylformamide[657] and in aqueous and aqueous–acetone solution,[650] 6 for Ga^{3+} [651,657,658] (a minimum of 4), 6 for In^{3+},[650] 3.9 for Sc^{3+},[659,660] 2.4 for Y^{3+},[659,660] 2.9 for Th^{4+},[659,660] 2 for Sn^{2+},[661] and about 4 for $UO_2{}^{2+}$ in aqueous mixed solvent systems[662,663] have also been obtained using the area ratio method.

A modified nmr technique has been proposed for the determination of the solvation number of metal ions in aqueous solutions consisting of a mixture of a salt of the metal ion under investigation and a very soluble salt of a metal ion with which the coordinated water has been shown to be labile.[664] Bulk and bound water peaks are still used to determine solvation numbers. From the values of the solvation numbers obtained for Al^{3+} and Ga^{3+}, evidence for contact ion pairing was obtained.

A method has been developed to determine hydration numbers which utilizes integral measurements of resonance signals.[665] The method has proven to be accurate for determining hydration numbers from measurements of the total hydrogen content of materials dissolved in D_2O. The requirements are that the materials contain some nonexchangeable protons and no paramagnetic ions.

The solvation of several paramagnetic ions have been studied in aqueous alcohol mixtures using selective broadening of the nmr absorption peaks of ethyl alcohol.[666] The solvation studies were conducted in deuterated ethyl alcohol solutions of $Cu(ND_3)_2 \cdot 3H_2O$, $CuCl_2$, $MnCl_2$, and $Cr(NO_3)_3 \cdot 9H_3O$ with varying amounts of D_2O added. From the ratio of amplitudes for the protons resonances of the CH_2 and CH_3 groups as a function of D_2O concentration, selective solvation was observed. A hydration number of 120 was obtained for the Cu^{2+} ion.

Proton relaxation time values as a function of salt concentration have been used to determine the hydration numbers of several cations and anions in alkali halide solutions.[667] Assuming the hydration number of the K^+ ion to be 6, hydration numbers for the following ions were obtained:

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Li, 1 ± 1; Na^+, 3.6 ± 1; Rb^+, 9.9 ± 2; Cs^+, 14.6 ± 2; F^-, 9.9 ± 2; Cl^-, 13.2 ± 2; Br^-, 16.2 ± 2; and I^-, 21.8 ± 2.

The correlation between relaxation time and salt concentration for methanol solutions of $CoCl_2$ and $CuCl_2$ and for aqueous solutions of HCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$ has been used to calculate solvation numbers for the cations and anions present.[668,669] The first shell solvation numbers determined for Co^{2+}, Cu^{3+}, and Cl^- ions in methanol are 4, 6, and 8, respectively.

Hydration numbers have been determined (±40%) for Li^+ (5), Na^+ (3), K^+ (1), Mg^{2+} (6), Zn^{2+} (12), Al^{3+} (16), Cl^- (2), OH^- (4), So_4^{2-} (5), and ice (−5; Broersma states that the value for ice is to be subtracted per monovalent ion) from proton relaxation time measurements using a modified Stoke's equation in the calculation.[670]

Hindman[671] has obtained effective hydration numbers for univalent cations and anions in aqueous solution from pmr chemical shifts. A solution model is adopted that subdivides the observed chemical shift produced by an ion into four terms: bond-breaking, structural, polarization, and electrostatic. In this interpretation the hydration of an ion is considered in terms of effective hydration numbers in which weaker interactions with a large number of water molecules are replaced by strong interaction with a limited number. Values of the effective hydration numbers of the following ions were obtained: Li^+ (4.0), Na^+ (3.1), K^+ (2.1), Rb^+ (1.6), Cs^+ (1.0), Ag^+ (2), F^- (1.6); Cl^-, Br^-, I^-, NO_3^-, ClO_4^- (all 0). Hindman[671] concluded that the concept of a complete hydration sphere of tightly bound water is not comparable with the data, and that the effectiveness of these ions in coordinating strongly with water decreases with increasing ionic radius. A structure-making effect is suggested by the data for the Li^+ ion while the larger halide ions tend to break down the water structure. The data also indicate that of the halide ions, only the F^- ion forms a hydrate in the chemical sense.

Swift and Sayre[672] have developed a technique for the determination of the primary hydration numbers of cations in aqueous solutions. The primary hydration number is defined as the number of water molecules associated with the ion for a time that is long compared to the time of diffusion, the method being applicable to those ions for which the average lifetime of an associated water molecule in the primary hydration shell is less than about 10^{-4} sec. This technique is based upon the kinetically distinguishable water molecule exchange with hydrated manganous ion and the relationship between pmr relaxation time and this exchange. In an aqueous electrolyte solution there are a number of different environments with which a water molecule might be associated: those associated with an anion; those in the primary hydration sphere of a cation; those associated only with other water molecules. Kinetically it might be possible to distinguish between these water molecules by adding to the solution another species or probe ion which is capable of reacting with water molecules. If the water molecules are kinetically distinguishable, the reaction will proceed as the sum of parallel reactions characterized by different rate constants. A "probe" species must satisfy the following conditions if this method is to be successful; it must react directly with water molecules; the rate constant for the direct reaction between the "probe" species and the water in a primary hydration sphere must be considerably different from the rate of reaction for all other types of water molecules; the lifetime of the "probe" must be relatable to a precisely measurable experimental quantity. The manganous ion was found to be a suitable probe. The technique involves a comparison of line widths obtained for two solutions, one containing a cation of known primary hydration number with the other solution containing the cation being studied. A common anion was present in each solution along with the "probe" manganous cation. An empirical formula was derived relating the ratio of water proton line widths to the primary hydration number of the cation studied

$$\frac{W_{AB} - W_A}{W_{AB'} - W_{A'}} = \frac{[H_2O]_{AB'} - N_{A'}[A']}{[H_2O]_{AB} - N_A[A]} \qquad (123)$$

where the subscript AB refers to a solution containing a standard cation of known hydration number, AB′ refers to a solution containing the cation being studied, and A and A′ refer to solutions of the same composition as AB and AB′ except containing no manganous ion. W_{AB}, W_A, $W_{AB'}$ and $W_{A'}$ are the line widths determined in a single comparison, [A] and [A′] are cation concentrations, $[H_2O]_{AB}$ and $[H_2O]_{AB'}$ are water concentrations, and N_A and $N_{A'}$ are the primary hydrations numbers of the two cations. This relation (eq 123) was tested with respect to temperature, anion, and concentration using the ions, Al^{3+}, Be^{2+}, NH_4^+, and H^+, whose primary hydration numbers are known. An application of this technique gave primary hydration numbers for the following cations: Mg^{2+} (3.8), Ca^{2+} (4.3), Sr^{2+} (5.0), Ba^{2+} (5.7), Zn^{2+} (3.9), Cd^{2+} (5.6), Hg^{2+} (4.9), and Pb^{2+} (5.7). A direct correlation between primary hydration number and ionic radius was found for the doubly charged series. The relatively low primary hydration numbers obtained by this method was interpreted as a reflection of the effect of water structure in determining the structures of hydrated ions.

Swift[673] has also determined the hydration numbers of the Ga^{3+} and Th^{4+} ions by the method just described. A value of 6 was obtained for the Ga^{3+} ion. The hydration number determined for the Th^{4+} ion was 10 ± 0.2, which is especially interesting with respect to the recently prepared[674,675] complexes of thorium with a coordination number of 10. The hydration numbers for both Ga^{3+} and Th^{4+} were found to be temperature independent. Line-width measurements as a function of temperature for aqueous solutions of the Ni^{2+} ion were used by Swift and Weinberger to obtain a solvation number of 6 for this ion.[676]

A discussion of the validity of the method developed by Swift[664] for the determination of primary solvation numbers of cations has been presented in the literature by Meiboom[677] as well as the rebuttal argument of Swift.[678]

Proton chemical shift measurements of aqueous solutions of Co^{2+} and histidine have been used to estimate the number of first hydration sphere sites of Co^{2+} that are utilized by a

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ligand and, therefore, are not accessible to water.[679] Since the pmr of coordinated and free water is a single resonance signal at constant Co^{2+} concentration, displacement of water by another ligand, histidine, causes a shift in water pmr toward the cobalt-free resonance line. This shift is used to estimate the number of available sites.

Pmr shifts in aqueous solutions of paramagnetic metal ions have also been used to determine the number of sites in the first hydration shell of Co^{2+} which are occupied by water.[680] The chemical shift produced by the presence of paramagnetic ions in solution can be related to the coordination number of the metal ion by the equation

$$\Delta\omega = pq\omega_{\mathrm{I}}[S(S+1)g|B|/3kt\nu_{\mathrm{I}}]A \qquad (124)$$

where q is the coordination number and p = [M]/[H_2O]. Introduction of a ligand into the metal ion solution causes the displacement of water from the first hydration sphere, thereby producing a difference in chemical shift as compared to the ligand free solution. Plots of water proton shift *vs.* [Co^{2+}] for solutions with and without an excess ligand (NaH_2PO_4) added were linear. In the phosphate solution the slope was 0.83 times as great as that for the ligand free solutions. Therefore, assuming the coordination number of CO^{2+} to be 6, one water site is then occupied by a phosphate group. Similar results were obtained for RNA–Co^{2+} solutions; Co^{2+} binds to one phosphate of RNA.

Schaschel and Day[681] have studied ion solvation in nonaqueous solutions using a pmr technique that involves measuring the proton chemical shifts of molecules such as tetrahydrofuran, diethyl ether, and triethylamine as they are added to a solution of sodium tetrabutylaluminate in cyclohexane. Evidence for a four-coordinated sodium ion was obtained with tetrahydrofuran while the data indicate a 1:1 complex for sodium–diethyl ether and sodium–triethylamine.

The solvation number of the electron in liquid ammonia has recently been calculated to be in the range of 20–40 for a dilute solution of potassium in liquid ammonia.[682] From an analysis of the contribution to the proton line shape from N^{14} spin lattice relaxation, the range of the solvation number was determined.

III. Evaluation

The results presented in this review indicate that, as one referee commented, the field is in a state of confusion. To some extent the confusion is more imaginary than real because the solvation number determined for any ion depends upon the method of measurement. For example, mobility measurements indicate the number of molecules moving with the ion while dielectric constant measurements indicate the number of molecules in the first sheath. However, a real source of confusion resides in the fact that there is no standard reference ion; consequently, in many instances the solvation number determined depends upon the reference ion and its assumed solvation number. The above statement is obvious since most methods measure the total solvation of the electrolyte and not that of the individual ions. One purpose of writing this review was to call attention to the state of the field at this time in hopes that it would have some heuristic value. There can be little hope of reconciling the results of different methods of measurement until there is definite knowledge of the structure of solutions and of the structure of solvations. That the possession of this knowledge is not imminent is testified to by the many models of the structure of solutions and solvation ions currently appearing in the literature.

With respect to the individual methods the following comments can be made. With mobility measurements one would obtain erroneous results for ions whose sizes as determined in solution are small compared to the particles of the medium, because of the limitation of Stoke's law. However, one must bear in mind that ion size as measured by X-ray diffraction on crystals is not necessarily the same as that of the ion in solution, and, therefore, there is no *a priori* way of determining whether Stoke's law applies from just a consideration of X-ray determined ion sizes. Bockris[558] indicates that the measurement of solvation by mobility measurements would be smaller than is the actual case because of the loss, arising from Brownian motion, of solvent molecules attached to the ion. Mobility measurements determine the total number of solvent molecules transferred through the solution by the ion. Solvation numbers determined by these methods will in general be greater than those determined by methods giving the number of molecules in the first solvation shell. Krishnan and Friedman[683] point out that while the study of transport coefficients of aqueous systems produce results that may be interpreted in terms of solution structure effects, the molecular theory of transport coefficients is so difficult that it would seem impossible to use such data to distinguish among the various models proposed to explain these same structural effects.

It has also been shown that spectroscopic and diffraction methods which are so often used for structural problems prove to be indecisive in determining absolute solution structure because these methods yield structure data which are averages over the contributions of various structures.[683] This difficulty results primarily from the short lifetimes, about 10^{-12} sec, that characterize the hydrogen-bonded structures in hydrogen-bonding solvents and their solutions.[683] Raman and ir methods are further complicated by spectral band components arising from both ion–ion and ion–solvent interactions because high concentrations are required for sufficient intensity. The interpretation of nmr relaxation data also suffers from the same limitation as that described above for transport coefficients.[683] Another weakness of nmr methods is that, in general, structural models are used that ignore the anion.

An excellent critical review of extrathermodynamic assumptions is in the literature,[684] and the authors would refer the reader to this paper for further comments on thermodynamic measurements.

Since the completion of this manuscript, we have been informed of an interesting paper[685] on the calculation of the heats and entropies of hydration using various models. The paper includes the evaluation of various methods for the determination of solvation numbers.

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