IONIC SOLVATION

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In spite of much experimental work, the significance of the term " solvation number " has remained indefinite. This is partly because the various experimental methods of determination apparently give considerable differences in numerical values (Table I), and so have provided but little incentive to the calculation of absolute solvation numbers. Consequently, more recent theoretical work on solvation has been directed principally to the calculation of solvation energy, because this quantity is open to less ambiguous experimental determination than are the solvation numbers.

Knowledge of absolute solvation numbers is of great importance in several ways. Such values are necessary to further the model of an ionic solution and for many detailed purposes ; for instance, the theory of concentrated electrolytic solutions awaits a knowledge of solvation numbers of definite significance. The large range of experimental phenomena which have been examined in attempts to determine solvation numbers experimentally illustrates the widespread influence of ion–solvent interactions. These phenomena include : refractivity, freezing and boiling points, vapour pressure, surface tension, density, specific heat and compressibility of ionic solutions, transport number of ions, and solubility of non-electrolytes in the presence of electrolytes. Lastly, a need exists for the calculation of solvation numbers in the theory of reactions in solution.

The object of the present work, therefore, is more closely to define the term " solvation number " and to attempt, from a critical discussion of the results of the literature, to find some order in the apparent chaos of conflicting results existing there.

Former Concepts of Ionic Solvation

In the earliest concepts of ionic solvation, ions were regarded as chemically bound to water molecules, forming hydrates in aqueous solution. This concept was supported by observations quoted by S. Aschkenasi [1] upon the sudden changes of conductivity, cryoscopic constants, etc., with solution composition which he regarded as corresponding to the formation and decomposition of various definite hydrates.

K. Fajans's consideration [2] of the polarisability of water molecules and the difficulty of substantiating the existence of definite hydrates in solution led to the concept that the interaction energy in solvation was entirely coulombic and did not involve covalent links. The molecules in the solvation sheath were regarded as continually interchanging with those in the bulk of the solution. M. Born [3] showed that the value of the solvation energy arising from a very simplified interpretation of this model for univalent

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[1] *Z. Elektrochem.*, 1922, **38**, 106.

[2] *Deut. physikal. Ges.*, 1919, **21**, 709.

[3] *Z. Physik*, 1920, **1**, 45.

salts was in substantial agreement with experiment. Some objection is made to the Fajans–Born concept of electrostatic solvation on the grounds that it would imply that the sequence of ionic velocities of a series of ions would be the same in different solvents, whereas this is not always the case.[4] This criticism was made before the possession of a " structure " by most polar solvents was realised; a consequence of this structure is that the steric properties of an ion become important in determining its solvation, so that the order of the ionic velocities for a given series of ions might be different in different solvents owing to the difficulty of an ion having a radius greater than some critical value " fitting into " the structure of certain solvents.

So long as the simpler ions of Groups IA and IIA of the Periodic Table and the halogens are considered, it seems probable that the success of the electrostatic theory of solvation energy implies that the ion–solvent interaction is almost entirely coulombic and that other types of interaction are not important in this connection. This conclusion is less certain for more complicated ions, *e.g.*, for those of Group VIII, where strong co-ordinating power tends to favour covalent attachment between ions and solvent. There exists little quantitative evidence on the solvation of these ions.

Acceptance of a coulombic view of the solvation of simple ions does not suffice for a satisfactory definition of solvation. It follows from the Born–Fajans concept that a certain number of solvent molecules will be firmly attached to the ion and that a further ion–dipole interaction takes place involving solvent molecules outside the inner ion–solvent entity. It may be suggested that the term " primary solvation " is used in reference to the attachment of solvent molecules to ions in solution for which (i) the ion and its attached solvent molecules move together as one entity during electrolytic transport; (ii) the solvent ions have completely lost their own separate translational degrees of freedom. " Secondary solvation " may be suggested as the term referring to all electrostatic interactions which are not included in the definition of primary solvation given above. The term " total solvation " would then refer to the sum of these two types of solvation. It has been suggested [5, 6] that " chemical " and " physical " should be respectively the description of " closely " and " loosely " attached solvent molecules. The term " chemical " appears, however, to be misleading when referring to coulombic solvation.

A quite different theory of ionic solvation from the general electrostatic theory of Fajans [2] was proposed by F. A. Lindemann,[7] who suggested that no permanent solvation sheath existed in solution, and that the solvent transport during movement of an ion is caused by the transfer of momentum from the ion to the solvent molecules with which it collides. Greater transfer of momentum would be expected with smaller than with larger ions, as is experimentally found. On this basis it was possible to explain the depen-

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[4] C. A. Krass, " Properties of electrically conducting systems ", 1922, p. 203.

[5] H. Ulich, " Hand- und Jahrbuch der chemischen Physik ", 1933, **6**, ii—iii, 186.

[6] *Idem, Z. Elektrochem.*, 1930, **36**, 504; cf. also J. Baborovský, *Chem. Listy*, 1934, **28**, 242; *Z. physikal. Chem.*, 1934, **168**, *A*, 135.

[7] *Trans. Faraday Soc.*, 1927, **23**, 387.

dence of the temperature coefficient of conductance upon ion size. No other independent evidence supports Lindemann's theory, which probably concerns a secondary effect (see below).

Choice of Concordant Experimental Methods for the Investigation of Primary Solvation

The discrepancy between the results of various experimental methods is exemplified in Table I by values from the literature for the sodium ion.

TABLE I

Values of the hydration number of the sodium ion at infinite dilution by various experimental methods

Method.	Hydration number.
Mobility (H. Ulich [8])	4
Water transport (M. Brull [9])	3
Mobility (E. H. Riesenfeld and M. Reinhold [10]) . .	71
Dialysis (H. Brintzinger [11])	17
Partial molar volume (E. Darmois [12])	1
Polarimetric (0·5N) (M. Cordier [13])	700 approx.*

These typical large discrepancies imply that different experimental methods give a measure of different types of solvation. As the methods are roughly divisible into those giving lower (< 10) and higher values (> 10) of solvation numbers, it is probable that the former give a measure of primary and the the latter a measure of some part of total solvation.† To elucidate this supposition, critical aspects of the main methods will be discussed; for which purpose they may be divided into the following groups according to the property measured: (i) Ionic and solvent transport, (ii) activity of solvent, (iii) activity of non-electrolyte solute, (iv) ionic entropy, (v) density of solutions, (vi) miscellaneous properties.

Difficulties in Methods.—A difficulty common to all methods except Ulich's ionic mobility method [8] and P. Debye's proposed supersonic e.m.f. method [14] is that of dividing up the solvation of the salt between its ions. Some workers [15] have assumed that large organic ions such as $Ph{\cdot}NH_3^+$ possess zero solvation numbers. Less justifiable assumptions (*e.g.*, that

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[8] *Trans. Faraday Soc.*, 1927, **23**, 392.

[9] *Gazzetta*, 1934, **64**, 624.

[10] *Z. physikal. Chem.*, 1909, **66**, 672.

[11] *Z. anorg. Chem.*, 1935, **223**, 101.

[12] *J. Phys. Radium*, 1941, **2**, 2.

[13] *J. Chim. physique*, 1946, **43**, 54.

[14] *J. Chem. Physics*, 1937, **5**, 13; cf. also Oka, *Proc. Math. Phys. Soc. Japan*, 1933, **15**, 415.

[15] *E.g.*, H. Remy, *Trans. Faraday Soc.*, 1927, **23**, 381.

* From the value 1111 for NaCl (see p. 179).

† Methods which measure more than the primary solvation would be expected to show less mutual agreement than those which measure the primary solvation, because of the less definite nature of secondary solvation. Moreover, some methods, *e.g.*, the salting-out method, doubtless depend upon other factors than the interaction between ion and solvent.

solvation of NO_3^- [16] and of I^- [17] is zero) have been made by other workers. The most reasonable method appears to be division in the ratio of the ion sizes, based upon some salt such as potassium fluoride, where the ionic radii are nearly equal.

Principal Methods.—The method of *ionic or solvent transport* includes several distinct approaches. The inert-reference-substance method [18, 19] is the best known. The fundamental assumption of this method is that the reference substance does not move under the influence of the applied field. P. Z. Fischer and T. E. Koval,[20] however, have recently reported the transport of raffinose under these conditions. It also follows that a local change in concentration of the reference substance would occur in the vicinity of the ion (salting-out).

In the Remy–Baborovsky method [21] of water transport, the liquid is intended to pass through a thin membrane between catholyte and anolyte and thus indicate the net volume change arising from the different solvation of cation and anion. The principal objection to this method is the probable inclusion in the measured water transport of water which is transported by a transfer of momentum from ions to molecules in the manner suggested by Lindemann [7] (streaming effect, cf. Ulich [6]). Values of solvation number resulting from the method would therefore be too high. Other difficulties of the method exist. For instance, there is a considerable volume change in the catholyte and anolyte caused by reactions at the electrodes. Some correction for this term has been attempted by H. C. Hepburn.[22] Further, the method is experimentally of doubtful validity because below concentrations of 1N. the effect of electroendosmosis at the membrane is considerable. It follows from the above that the Remy–Baborovský method measures some part of the total rather than the primary solvation, and this conclusion is doubtless also valid for Jander's diffusion method [23] and Brintziger's

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[16] F. Bourion *et al.*, *Compt. rend.*, 1937, **204**, 1420.

[17] M. Cordier, *ibid.*, 1942, **142**, 707.

[18] G. Buchböck, *Z. physikal. Chem.*, 1906, **55**, 563.

[19] E. W. Washburn, *J. Amer. Chem. Soc.*, 1909, **31**, 322.

[20] *Bull. Sci. Univ. Kiev*, 1939, No. 4, 137.

[21] H. Remy, *Z. physikal. Chem.*, 1915, **89**, 529; J. Baborovský, *Rec. Trav. chim.*, 1923, **42**, 229; H. Remy, *Z. physikal. Chem.*, 1925, **118**, 161; 1926, **124**, 394; Baborovský, *ibid.*, 1927, **129**, 129; J. Baborovský and J. Velišek, *Chem. Listy*, 1927, **6**, 227; H. Remy and H. Reisener, *Z. physikal. Chem.*, 1927, **126**, 161; A. Wagner, *Chem. Listy*, 1927, **21**, 543; Baborovský, Velišek, and Wagner, *J. Chim. physique*, 1928, **25**, 452; Baborovský and Wagner, *ibid.*, p. 452; *Chem. Listy*, 1929, **23**, 97; Wagner, *ibid.*, p. 349; 1931, **25**, 349; H. C. Hepburn, *Proc. Physical Soc.*, 1932, **44**, 267; Baborovský and Wagner, *Coll. Czech. Chem. Comm.*, 1931, **3**, 53; Baborovský, O. Viktorin, and Wagner, *ibid.*, 1932, **4**, 200; Baborovský, *Arhiv Hemiju*, 1932, **6**, 85; Baborovský and Viktorin, *Coll. Czech. Chem. Comm.*, 1932, **4**, 155; 1933, **5**, 518; Wagner, *Chem. Listy*, 1933, **27**, 481; Baborovský and Viktorin, *ibid.*, 1934, **28**, 168; Baborovský, *ibid.*, 1936, **30**, 5; Baborovský and G. Koudela, *ibid.*, 1938, **32**, 5; Baborovský, *Trans. Electrochem. Soc.*, 1939, **35**, 13.

[22] *Phil. Mag.*, 1938, **25**, 1074.

[23] G. Jander and A. Winkel, *Z. physikal. Chem.*, 1930, **149**, 97; H. Brintziger and C. Ratanarat, *Z. anorg. Chem.*, 1935, **222**, 113; G. Jander and H. Mohr, *Z. physikal. Chem.*, 1942, **190**, *A*, 81.

dialysis method,[11] for both these methods give high results, usually of the same order as those obtained from Remy's method.

Ulich's ionic mobility method [8] appears to measure a more definite quantity than the above methods, because it obtains directly the volume of the solvated ion from an application of Stokes's law to ionic mobilities at very low concentrations, so that the number of water molecules which migrate permanently attached to the ion (primary solvation number) is obtained. The method is somewhat limited by the non-applicability of Stokes's law to some ions in aqueous solution.[24] Other objections recorded in the literature appear to have little force ; for instance, the use of crystal radii for calculating the volume of the ion in the solvent sheath involves some loss of accuracy but the difference between crystal ionic radii evaluated by several methods are not large enough to make this a serious one. The appropriate volume of the solvent molecule to use in the evaluation of the solvation number is somewhat more indefinite. Owing to the high pressure in the vicinity of the ion, and the inhibition of rotational degrees of freedom of the dipoles attached to the ion, the molecular volume, calculated in the usual way, is too large. Calculation of the solvation number on the basis of an arrangement of close-packed spheres with the usual (uncompressed) volume for the solvent molecule was taken by Ulich to give a lower limit for the solvation number. The true value should be higher than this because of electrostriction of the solvent molecules in the neighbourhood of the ion, and assuming arbitrarily that this caused the solvent volume to be reduced to about half its original value, Ulich calculated an upper limit for the solvation number. The values accepted here from the method are the mean of these two estimates.

Methods depending upon *Activity Determinations, e.g.*, cryoscopic,[25] vapour pressure,[26] and salting-out,[27] all give relatively high results, but are similar in representing a " total interaction effect ", and would therefore be expected to measure both primary and secondary solvation, which view accords with the high results obtained. The cryoscopic method [25] appears to be of doubtful validity because the results depend upon the non-electrolyte used ; *e.g.*, acetone and paraldehyde show unreasonable results, whilst resorcinol appears to function satisfactorily. The theory by means of which the results are evaluated is extremely inadequate and a satisfactory theory for the complicated systems used would be very difficult. The change in solubility of gas or solid upon the addition of

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[24] Cf. G. Kortüm, " Lehrbuch der Elektrochemie ", Leipzig, 1948, p. 130.

[25] F. Bourion and E. Rouyer, *Compt. rend.*, 1933, **197**, 52 ; Bourion, Rouyer, and O. Hun, *ibid.*, 1933, **196**, 1015 ; Bourion and Rouyer, *ibid.*, p. 1111 ; 1933, **197**, 52 ; 1935, **201**, 65 ; Rouyer, *ibid.*, 1934, **198**, 742, 1490 ; Hun, *ibid.*, p. 740 ; Rouyer, *ibid.*, p. 1156 ; Bourion and Rouyer, *ibid.*, 1935, **201**, 65 ; Bourion and Hun, *ibid.*, 1936, **202**, 2149 ; Hun, *ibid.*, p. 1779 ; Bourion, Rouyer, and Hun, *ibid.*, 1937, **204**, 1420 ; F. H. Getman, *Rec. Trav. chim.*, 1937, **56**, 1025 ; Bourion and Rouyer, *Compt. rend.*, 1937, **205**, 662 ; Bourion and Hun, *ibid.*, 1937, **204**, 1872 ; Bourion and Rouyer, *ibid.*, 1938, **206**, 1967.

[26] B. H. Van Ruyven, *Rec. Trav. chim.*, 1937, **56**, 111.

[27] P. P. Kosakewich and N. A. Ismailow, *Z. physikal. Chem.*, 1930, **150**, *A*, 308.

electrolyte has been used to obtain a measure of hydration on the assumption that the decrease in solubility on addition of a salt is due to a reduction in the activity coefficient of water.[27] This analysis is also over-simplified; a formally correct picture for very dilute solutions was given by P. Debye and J. McAulay.[28] Essentially, the simpler analysis omits to take account of the effect of the non-electrolyte solute on the dielectric constant of the medium. Values calculated from this method also depend upon the nature of the non-electrolyte [27] and cannot therefore be considered as valid for determination of ionic solvation. However, it is sometimes possible to make qualitative inferences regarding solvation from salting-out studies. For example, J. O'M. Bockris and H. Egan [29] found that for concentrations of sodium chloride between N/1000 and N (non-electrolyte solute: benzoic acid), the salting-out appears to decrease anomalously with decreasing dielectric constant in alcohol–water mixtures containing an excess of water. This fact can be explained if it is assumed that the sodium chloride is preferentially solvated with water.

N. Bjerrum [30] calculated solvation numbers from the activity of the solvent in a given solution. His method was considered by Ulich [5] to give primary solvation numbers, but it does not seem possible to draw this definite conclusion owing to the small number of ions to which the method has been applied. E. Schreiner,[31] using this method, found the improbable result of 11 for hydrogen chloride in this way. Further, R. H. Stokes and R. A. Robinson's use [32] of an improved form of this method to derive an empirical relation between the activity coefficient and concentration for electrolytes in relatively concentrated solutions involves some consequences concerning hydration which are contrary to the general trend of results obtained by other methods in dilute solutions.

The *entropy* decrease occurring when gaseous ions undergo solution in water at infinite dilution can probably be used to calculate primary solvation numbers because it depends upon the "freezing up" of the degrees of freedom of the water molecules near the ion.[33] The assumption is made that the entropy decrease when water is transferred from the bulk of the solution to the primary solvation sheath is the same as that on freezing water. Values from this method agree very well with those calculated from Ulich's ionic mobility method.[8] The entropy method can also be applied to the calculation of the solvation of non-electrolytes.[34]

Lastly, special interest has been attached to methods of determining solvation numbers from measurements of the *partial molar volume* of electrolytes at infinite dilution. J. D. Bernal and R. H. Fowler [35] refer to this method and its results as being particularly satisfactory, but give no

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[28] *Z. physikal. Chem.*, 1925, **26,** 23.

[29] *Experientia*, 1947, **3,** 11; *Trans. Faraday Soc.*, 1948, **44,** 151.

[30] *Z. anorg. Chem.*, 1920, **109,** 275.

[31] *Ibid.*, 1924, **135,** 333.

[32] *J. Amer. Chem. Soc.*, 1948, **70,** 1870.

[33] H. Ulich, *Z. Elektrochem.*, 1930, **36,** 497; *Z. physikal. Chem.*, 1934, **168,** 141.

[34] J. Kielland, *J. Chem. Educ.*, 1937, **14,** 412.

[35] *J. Chem. Physics*, 1933, **1,** 515.

details as to how it might be applied. Darmois [12] describes the procedure and results of this method for a large number of simple aqueous electrolytic solutions. It is clear that, as the method is concerned with the volume of the ion–solvent complex itself and not with the surrounding water molecules which are not firmly attached to the ion, it should measure the primary solvation. However, the results obtained are substantially lower than those of the other concordant methods for obtaining primary hydration numbers. The reason for this is not clear at present.

Other Methods.—These involve measurements of reaction velocity, the variation of the distribution of an electrolyte between two immiscible solvents, the *compressibility* of ionic solutions, and the use of *supersonic e.m.f.s.* The first method has been used recently by Cordier [13] and yielded extremely high results (of the order of 10^2). Such values sometimes imply that more water is used up in the hydration sheath than exists in the solution, *e.g.*, this is so for a solution containing 0·5 g.-ion/l. of sodium chloride, for which substance at this concentration the solvation number is 1111 according to Cordier.[13] The distribution method [31] is connected with several unsolved difficulties: the results of J. N. Sugden [36] and of E. Angelescu and O. Dutchievici [37] are discrepant, and Sugden's values yield negative solvation numbers for anions which were supposed to exert a "depolymerising effect" upon water, regarded by him as $(H_2O)_3$ in the liquid state. Measurement of *compressibility* [38] appears to be a satisfactory method of obtaining solvation numbers: results from it agree quite well with those of ionic mobility [8] and entropy [33] methods, and it seems probable therefore that this method also yields primary solvation numbers. This is supported by the concept that the solvent sheath in primary solvation is under very large pressure owing to the field near the ion, and therefore reaches a limiting value beyond which further compressibility is due to that of the bulk of the solvent. Lastly, Debye's theoretical treatment [14] of the p.d. produced in an electrolytic solution when it is subjected to supersonic vibrations appears to provide a method without objection in principle and yielding individual solvation numbers, as the e.m.f. produced is a function of the ratio of the masses of both positive and negative ion–solvent complexes in the electrolyte. The e.m.f. involved is of the order of 10^{-6} volt; so that measurements, which do not yet seem to have been attempted, are likely to be difficult.

The above survey shows, therefore, that the following methods probably measure primary solvation: Ionic mobility, ionic entropy, compressibility, and density. The agreement between these methods is relatively satisfactory, compared with the very considerable disorder which is apparent when the results of various methods are taken without discrimination (see Table I). Numerical results of these four methods are shown in Table II.

There is little experimental information concerning the concentration

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[36] *J.*, 1926, 1742.

[37] *Bull. Soc. chim. Romania*, 1932, **14**, 46.

[38] A. L. T. Moesveld and H. T. Hardon, *Z. physikal. Chem.*, 1931, **155**, *A*, 238; A. Passinski, *Acta Physicochimica*, 1938, **8**, 385.

variation of solvation which is small for methods measuring primary solvation (contrast the large concentration variation given by the cryoscopic [25] and the water-transport methods [21]).

TABLE II

Results of experimental methods giving primary solvation numbers at infinite dilution

Ion.	Mobility.‡ (1.)	Entropy. (2.)	Compressibility.† (3.)	Density. (4.)	Mean of (1, 2, 3, 4).	Mean of (1, 2, 3).
Li^+ . . .	5	5	3	2	4	4
Na^+ . . .	4	4	4	1	3	4
K^+ . . .	4 *	2	3	0	2	3
Rb^+ . . .		2		0	1	2
F^- . . .		5	5		3	5
Cl^- . . .	4 *	2	3	0	2	3
I^- . . .	0·7 *	0·5	2	0	0·7	0·6

* Extrapolated for aqueous solutions from some results in alcoholic solutions, Stokes's law not being applicable in aqueous solution of these ions.

† Calculated for individual ions on the approximate basis that K^+ and Cl^- are equally hydrated.

‡ Mean of upper and lower limit values.

Summary.—(1) Previous concepts of ionic solvation are discussed, and the definition of two types of solvation, primary and secondary, is given.

(2) A critical discussion of the experimental methods for the determination of solvation numbers shows that there are several methods of measuring "primary hydration numbers" which give concordant and rational values.