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IONIC SOLVATION

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Abstract

The concept of ionic solvation and the way it has been presented in the literature is critically discussed.

Key words

Ionic solvation, ionic hydration, electrolytes

The evolution of the concept of ion solvation

The concept of ionic hydration, an example of ionic solvation, where the solvent is water, was firstly introduced when Kablukow [1] said, in 1891: "In my opinion, water, as it decomposes the molecules of the dissolved substance, forms with the ions unstable compounds which exist in a dissociated state".

MacInnes [2] in 1939 defines solvation as:

"...complex formation between the solute and the solvent. With aqueous solutions it is called *hydration*. ..."

When defining total ionic solvation as a set of predominantly coulombic interactions between the solvent molecules and a certain ion, Bockris [3], in 1949 admits two types of solvation, primary and secondary:

"Acceptance of a coulombic view of the solvation of a simple ion 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. ..."

We should note that trying to characterise ionic solvation and on the basis of coulombic ion-solvent interactions, this author [3] mentions previous ideas on the matter:

"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 [4, in 1922] 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 considerations [5, 1919] of the polarisability of water molecules and the difficulty of substantiating the existence of definite hydrates in solution lead to the concept that the interaction energy in solvation was entirely coulombic and did not involve covalent links. ..."
"... It has been suggested [6,7] 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."

According to Bockris [3], Lindemann [8] in 1927, has the following point of view on ionic solvation:

"... 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. ..."

On the other side, Gurney [9], in 1953 presents solvation as follows:

"The interaction that takes place when an ion is introduced into a solvent is called the *solvation* of the ion. In recent years the concept of solvation has gradually changed. Formerly, solvation was held to be the attachment of a large or small number of solvent molecules to an ion; and *heat of solvation* meant the heat evolved in the process of attachment. It is now felt that for most species one cannot properly distinguish between solvent molecules that are attached to an ion and those which remain unattached. It is much more useful to use the word *solvation* to denote the total interaction between an ion and a solvent."

Miller [10], in 1956 says, concerning Robinson and Stokes [11] 1948 model for strong electrolytes, the following:

"... The basic idea is that instead of consisting of bare particles dissolved in a certain quantity of solvent, the solution really consists of solvated particles dissolved in the remaining "free" solvent. Since the outer

surface of the solvated particle consists of solvent molecules, the solvent-solvated solute interactions are essentially reduced to solvent-solvent interactions. Thus the heat of solution of a solvated particle will be practically zero. In the case of an ion, the orienting effects on a polar solvent which would alter the local dielectric constant are now contained in the solvation sphere, and consequently the *solvated ion* essentially sees only the macroscopic dielectric constant of the solvent. Hence as far as solute-solvent interactions are concerned, the hydrated solute should form practically ideal solutions with the solvent. ..."

However, in 1957 Frank and Wen [12] advance new concepts suggesting three different regions, A, B and C, surrounding the solvated ion:

"The innermost (region A) is one of immobilization, the second (region B) one in which the water is less ice-like, i.e. more random in organization, than "normal", and the third (region C) contains normal water polarized in the ordinary way by the ionic field which, this far out, has become relatively weak. The cause of the structure-breaking (cf. Gurney [13]) is presumably the approximate balance in region B between two competing orienting influences which act on any given water molecule. ..."

The above model comes from research on the thermodynamic and transport properties in electrolyte solutions from several authors [12] and led to the classification of the ions into "structure-formers" and "structure-breakers":

"... At any rate, it is possible to make entropy data the basis for assigning an orderly gradation of net structure-altering influence to a considerable number of ions. According to this, cations smaller or more highly charged than K^+ are net structure-formers, and become more strongly so the smaller and the more highly charged. K^+ is slightly structure-breaking on balance, and this tendency increases through Rb^+ and Cs^+. F^- is a structure former, and the other halide anions are structure-breakers, increasing in this tendency with size. NO_3^- and ClO_4^- are strongly structure-breaking, and SO_4^{2-} less so. OH^- seems to be a structure-former."

The following Bockris [3] indications,

"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 difference in numeric values .... 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..."

are somehow contested by Samoilov [14]:

"A division of the total effect of hydration of ions into two parts is undoubtedly advisable. What should be rejected, however, is the interpretation of the "primary" hydration as a firm binding by the ion of the water molecules. At the same time it seems more correct to apply to these parts of hydration not the terms "primary" and "secondary", but "close" and "far" ...

Concerning the difficulties found when describing quantitatively the individual ion hydration through "hydration numbers", Samoilov [14] contests "the concept of ion-binding of a certain number of water molecules of a solution".

He then suggests:

"What is needed is to develop a more general approach to the study of the hydration of ions in solutions, which would in no way be based on the concept of the binding, by ions, of a certain number of water molecules. On the contrary an elucidation of the problem of binding molecules of water of the solution by an ion should follow from such an approach only as a consequence. Such an approach should be applied both to relatively weak interaction of ions with water, and to a stronger interaction which, possibly (in the limiting case) leads to the binding, by the ion, of the water molecules.

Therefore, Samoilov [14] presents a dynamic model based on the time a water molecule is bound to the ion:

"Let us consider the translational motion of water molecules in a diluted aqueous solution of electrolyte. If a molecule of water is in the immediate vicinity only of water molecules, then let it spend an average time τ in the immediate vicinity of a certain selected molecule. The value τ is the mean time during which two molecules which have become immediate neighbours remain in the immediate vicinity of each other. Let the value of the activation energy of exchange be E. The values τ and E are close to the corresponding values for pure water. ... However, the mean time that a molecule is in the immediate vicinity of the ion is not τ since an ion is, energetically, not equivalent to a molecule of water. Let the mean time that a water molecule is in the closest equilibrium position to the ion in the structure of the solution be equal to a certain τ_i. The fact that $\tau_i \neq \tau$ is connected chiefly with the change (due to the influence of the ion) of the value of energy of activation of the exchange of the closest molecules: in place of E, this value becomes E + ΔE.

It may be stated that the values τ_i/τ and ΔE are truly general quantitative characteristics of ion

hydration in solutions. Indeed, if an ion firmly binds the immediate molecules of water, then the ratio τ_i/τ is great. For a limiting case (permanent binding), $\tau_i/\tau = \infty$. A reduction of the value τ_i/τ signifies a weakening of the bond of the ion with the immediate water molecules of the solution. The ratio τ_i/τ is connected with the value ΔE by an extremely simple relation $\tau_i/\tau = \exp(\Delta E/RT)$. Thus, the problem of a quantitative description of ion hydration in a solution reduces to the finding of the value ΔE for this ion. ..."

"When ΔE > 0 the magnitude of the ratio τ_i/τ > 1, i.e., a molecule of water spends on the average more time in the immediate vicinity of an ion than in the immediate vicinity of a water molecule in water. Thus, there occurs something in the nature of a certain "effective binding" by the ion of the immediate molecules of water. Of special interest is the case ΔE < 0. In this case, the value τ_i/τ < 1, and, thus, the molecule of water near the ions become more mobile than in pure water. This phenomenon was called "negative hydration".

"Now it is quite understandable why special difficulties arose in attempts to describe the hydration of ions by means of hydration numbers for ions K^+, Rb^+, ... Indeed, if for ΔE > 0 one may still speak of ion-binding of water molecules of a solution, then when ΔE < 0 such an approach is void of all meaning."

In 1970, Bockris [15], summarises the previous ideas:

"The meaning of hydration numbers.

If the time an ion waits near a water molecule is long compared with the average time a water molecule takes to orient into association with an ion, then the probability of the water molecule's being captured by the ion is high. That is, the probability of an ion's capturing a water molecule depends on the ratio $\tau_{ion\ wait}/\tau_{water\ orient}$.

If $\tau_{ion\ wait}/\tau_{water\ orient}$ is large, then the ion will be surrounded by the full geometrically permitted complement of bonded water molecules *during all its zig-zag motions* through the solution. Under these circumstances, the hydration number (i.e., the number of water molecules which participate in the translational motions of the ion) will be equal to the coordination number.

If, however, $\tau_{ion\ wait}/\tau_{water\ orient}$ is of the order of unity, then the situation is interesting. The time an ion spends in the neighbourhood of a water molecule is of the order of the water reorientation time, and, hence, though the ion is not sure to capture a water molecule, there is a certain probability, less than unity. At the same time, one must consider the opposite process: An ion with a bound water molecule collides with a water molecule belonging to the water network. There will be a certain probability that the ion will lose its water to the water network. But there are plenty of water molecules all around and the ion has a chance of making up its loss.

Thus, over a period of time which is long compared with the period of contact between a moving ion and a specific water molecule, the ion has aligned and trapped in its field a certain number of water molecules which is less than the number of water molecules which geometrical close packing makes possible, i.e., the coordination number.

The collisions between ions and water molecules inked to the water network are analogous to any other collision process. Consider, for example, the collisions between neutrons and U^{238} nuclei, in which slow neutrons stand a better chance of being captured than fast neutrons. One says that there is a large capture cross section for slow neutrons. It is as if a slow moving neutron sees a bigger target than a fast moving one.

What happens if the ions wait for so short a time that, even before a water molecule has had time to break out of the water structure and turn around, the ion has hopped away ? Then, the probability of a water molecule's being captured by the ion is zero, and, on a time average, the ion will not have any *aligned* water molecules in contact with it, i.e., its primary hydration sheath is empty. This does not mean that such ions are not surrounded by interacting solvent molecules or that they would have no coordination water. It only means that, because $\tau_{ion\ wait}/\tau_{water\ orient} \ll 1$, the ion does not wait long enough at any particular site for contiguous water molecules to swing out of the water network into minimum-energy orientation with the ion. Even if the ion does capture a water molecule, it is bound to lose it soon. It also means that the moving ion exchanges water molecules so easily with the surrounding solvent that, in effect, the moving ion does not carry its sheath along with it. Its solvation number is zero, though its coordination number is that dictated by geometry.

The picture of solvation numbers presented here is a dynamic one. The solvation number refers to the number of water molecules which remain aligned with the ion *during* its jumps through the medium. But it is not necessary that the same individual water molecules serve in the solvation sheath for an indefinitely long time. A given water molecule may serve the ion for some time, but it is not imprisoned for life in its hydration shell. A chance collision, and the particular water molecule may link up again with the water network, get left behind by the hopping ion, and watch another water molecule yield to the attraction of the ionic field and be incorporated in the primary solvation sheath.

Why is the concept of solvation numbers useful ?

In all this dynamic exchange of solvent molecules between the coordination region and the main bulk of solvent, has the concept of solvation number any utility ? Yes, the solvation number can be considered the *effective* number of solvent molecules to be "permanently" bound to the ion and to follow its motion from site to site. The kinetic entity is not the bare ion but the ion plus the solvation number of water molecules."

Also, Bockris [15] distinguishes solvation number and coordination number in the following way:

"... Coordination number, i.e. the number of nearest-neighbor water molecules which are in contact with or coordinate or surround an ion. ..."

Bell in 1958 [16] refers to the limitations of an electrostatic model for the ion-solvent interactions involving the dielectric constant ε as follows:

"Unfortunately the concept of hydration was often used with more enthusiasm than discrimination, and little attempt was made to define clearly what it implied. In particular, hydration was frequently invoked simply as a convenient means of accounting for discrepancies between observed properties and those predicted by some theory of solution of doubtful validity, rather as "association" was used to explain discrepancies in the behaviour of solutions of non-electrolytes. ...

In the period 1920-40 the great successes of the interionic attraction theory in accounting for the properties of very dilute solutions of electrolytes produced a considerable prejudice in favour of "physical" rather than "chemical" theories of solution, solvation being placed in the latter class. However, it has become increasingly evident that consideration of the immediate surroundings of ions in terms of electrostatic theory is not really profitable. For example, Born's well known expression [17] gives the electrostatic energy of an ion in a medium of dielectric constant D as e^2/Dr (where e = charge and r = ionic radius). If this is to be applied logically, however, it is quite incorrect to use the ordinary macroscopic value of D, since the solvent in the immediate neighbourhood of the ion is subject to enormous electrostatic fields and hydrostatic pressures, which will greatly modify the effective value of D. No exact theory of these effects is available, and the "effective dielectric constant" thus approaches the status of an indefinitely adjustable parameter. Under these conditions "physical" treatment has no advantage over "chemical" treatment as a means of representing the interaction between the ion and the solvent. This difficulty does not arise when considering the variation with concentration of properties of dilute solutions, as in the successful applications of the interionic theory. It does, however, affect any attempt to account for the properties of different salts or of solutions in different solvents, and also any treatment of concentrated solutions."

He [16] later says:

"... modern methods of investigation have provided a clearer understanding of the nature of liquid water, and on the way in which it can be modified by the presence of ions. In particular, it is recognized that although an ion can have some effect on water molecules at a relatively

large distance, molecules in its immediate neighbourhood will be bound particularly firmly: consequently it is often legitimate to distinguish between primary and secondary hydration. ..."

" ... The concept of a primary hydration number is useful only to the extent that a single number will account for a variety of properties of a given ion. All the molecules concerned will contribute to the effect of hydration on different properties, but the contribution of each will depend upon the particular property in question. ..."

The interpretation of the diffusion coefficients is cited as an example:

"... A somewhat similar, but more satisfactory, approach involves the interpretation of diffusion coefficients of electrolytes in concentrated solutions. ... Since both ions move in the same direction this method gives values for the sum of the two hydration numbers, and certain assumptions are needed to obtain the individual values. It seems likely that only the first layer of water molecules will be bound firmly enough to move as a unit with the ion, so that primary hydration numbers should be obtained. ..."

Concerning thermodynamic properties Bell [16] says:

"... These have the advantage that the underlying theory is better understood than that of transport phenomena: on the other hand, the later may give information about the interactions in the immediate neighbourhood of an ion, whereas study of any thermodynamic quantity necessarily gives an overall measure of the mutual interaction of all parts of the system. ..."

Concluding:

"... To sum up, it may be said that the concept of ionic hydration in solution is necessary in order to account for the individual properties of dissolved ions, and also for the behaviour of concentrated electrolyte solutions in general. The idea of a fixed primary hydration number is a useful first approximation in dealing with a number of properties, but a complete understanding of the problem must take into account the peculiar associated structure of water, and the effect of ions upon it even outside the primary hydration sphere. ..."

Also, in 1958, Harned [18] suggests that ion-solvent interactions may lead to "localized hydrolysis":

"... But this kind of ion-solvent interaction can also lead to a "localized hydrolysis" by reaction with anions which are proton acceptors [19]. The protons in

these water molecules will be repelled from the hydration sheath and will tend to form linkages with proton acceptors such as hydroxyl or acetate ions. This tendency may be represented by

$$M^+ + H_2O \rightleftharpoons M^+ \ldots OH^- \ldots H^+$$

where the dotted lines represent the linkages due to ion-solvent molecule forces. The interaction with a proton acceptor may be represented by

$$M^+ \ldots OH^- \ldots H^+ + A^- \rightleftharpoons M^+ \ldots OH^- \ldots H^+ \ldots A^-$$

and the proton regarded as oscillating between extreme positions on hydroxyl group and proton acceptor. Addition of these expressions gives

$$M^+ + H_2O + A^- \rightleftharpoons M^+ \ldots OH^- \ldots H^+ \ldots A^-$$
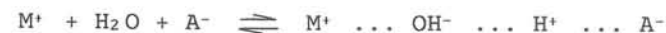
which resembles ion pair formation of the type

$$M^+ + A^- \rightleftharpoons M^+ \ldots + \ldots A^-$$

in that both lead to a reduction of the number of free ions in the solution. This mechanism leads to a lower activity coefficient than that calculated upon the basis of complete ionization, and this lowering will be greater the smaller the radius of the cation. Thus, for compounds of the proton accepting hydroxides, acetates, etc., the order of activity coefficients will be Cs > Rb > K > Na > Li. ..."

One year later, Stokes [20] adds:

"... It is obviously of the utmost importance to our understanding of electrolyte solutions that we should know what the kinetic entity which we call an ion is, whether it is the bare ion, or whether it carries with it water molecules sufficiently firmly bound to be regarded as part of the ion, and if so, how many such molecules. It must be admitted that we do not know with any great certainty, though the importance of the problem has been realized for 50 years or more. One difficulty is that it is not possible to state quite unambiguously what we mean by a water molecule being 'bound to the ion'.

There are a few cases where the inner sheath of water molecules is permanent in a long-term sense and the water molecules are firmly attached, possibly by coordinate links. ..."

"... Chromium and cobalt are transition elements with a marked tendency to form coordinate links. In the case of noble-gas type ions, and for any water molecules not in immediate contact with the ion, the forces involved are entirely electrostatic and no specific formula can be assigned to the aqueous ion. One may nevertheless hope to obtain an average value for the number of water molecules moving with the ion; such a value need not, of course, be

integral, since the actual number per ion may vary from one ion to another and for the same ion from time to time. The hydration may be far from permanent in the everyday sense of the word; the permanence implied is, rather, relative to the time-scale of the Brownian motion. ..."

"... It is seen that for all the alkali and halide ions except the smallest (Li⁺ and F⁻) this structural entropy term corresponds to a considerable increase of disorder, which is greatest for the largest ions. It appears therefore that beyond the first layer of water molecules there is a region where the water structure is broken down; it is pointed out that this could arise from the manner in which the first layer of water molecules is arranged. Round a positive ion, the water molecules would be oriented with all the hydrogens outwards; they could not, therefore, all participate in the normal tetrahedral water arrangement (even if the dimensions of the central ion were close to those of a water molecule) for this arrangement would require two of the water molecules to be oriented with the hydrogens inwards. Frank and Evans support their argument for this structure-breaking effect by a number of other considerations, notably of viscosity and heat capacity data. For polyvalent monatomic ions such as Al⁺⁺⁺, the entropy loss is much greater; part of this increase is ascribed to an extension of the "frozen" region to layers beyond the first. ..."

Samoilov [21] in 1967 reaffirms previous ideas:

"...It is becoming possible to see particularly clearly the relationship between the various characteristics of a solution, on which the short-range hydration of the ions depends (the coordination numbers of the ions, the orientation of the water molecules closest to the ion, the bonds which they form with the ion, and the state of the water beyond the limits of the first hydration sheath of the ion).
Any characteristic of the short-range hydration of ions in solution should be a quantity which is a function of ΔE_j. Only in this case will it reflect directly the strength of the bond between the ion and the water molecules making up its immediate environment in the solution. The more firmly the water molecules closest to the ion are bound to it (the stronger the short-range hydration of the ion), the less frequently does exchange take place between these molecules and the molecules of the rest of the water in the solution, joined by a network of hydrogen bonds. ..."

At the same time, Davies [22] shows the influence of "structure-former" and "structure-breaker" ions on properties of electrolyte solutions:

"... Indications that the structure of the solvent is looser in the local environment of an ion are a high mobility, a negative effect on the solvent's viscosity, and (other things being equal) a high ionic entropy. Most

of the common anions are structure-breaking, but the fluoride and hydroxide ions are ordering, and so are the acetate and some other organic anions in which the negative charge is localized on one oxygen atom. Multiply-charged ions in general are structure-producing, and the ions of the commoner metals like iron, copper, and nickel, with two charges and a small radius, can be looked on as a permanently hydrated by the sphere of adjacent water molecules that their co-ordination number enables them to accommodate; but to think of ion such as the sodium or calcium ion in this way is more dangerous, as their "hydrates" will have high "dissociation constants", and they will be more sensitive to changes in environment and conditions. ..."

Franks [23] elaborates on the meaning of the term "structure" for a liquid:

"... the term "structure", as applied to a liquid, must be placed in its right context. In liquid water the molecular reorientation time, resulting either from rotational or translational diffusion, is of the order of 10^{-11} sec, and if a dissolved solute can markedly lengthen this period, say to 10^{-10} sec, the effect can be referred to as structure promotion. Conversely, if the presence of the solute results in a shortening of the reorientation period, then this solute is termed as a structure-breaker. ..."

Berecz [24] adds:

"...On the basis of simplified geometrical considerations, the hydration numbers of ions of different size and charge have been determined and systematized, using literature data on the crystallographic and hydrated ion radii of ions which are common in electrochemical practice.
The systematization has led to the conclusion that the ions are positively hydrated as long as the crystallographic radius is less than the radius of a water molecule, i.e. 1.38 Å, or the coordination number of the ion for water is greater than 6.
Numerous physicochemical studies indicate that the hydrated ions affect water molecules located beyond the hydration sphere of ions, too. The number of water molecules present in the region of disturbed structure depends on the size, charge and the electron structure of the ion and it may exceed the hydration number by a factor of 1.2 - 2.4.
On the basis of the above conclusions the maximum number of water molecules with structure different from that of free water, i.e. the maximum hydration numbers, is given as a function of the atomic number for halide, metal and some complex negative ions, selected from the first sixty elements of the periodic system.
The correctness of our calculations has been confirmed by viscosity and vapour pressure data. It has

been concluded that electrolytes of different types can be systematized on the basis of hydration numbers. ..."

At the same time, Yeager [25] discusses the different hydration number values for the same ion when obtained from different methods:

"... A survey of hydration numbers listed in the literature shows that one can obtain any value from - 2 to + 20 by judicious choice of experimental technique. This large variation has two origins: (1) the primitive nature of the theory on which the estimates are based and (2) the fact that different measurements average over different types of interactions and different time scales. ..."

Groves [26] adds the following:

"...When a salt is dissolved in water the structure of the water is very considerably modified. A positive ion strongly attracts water molecules in such a way that the negatively charged oxygen atoms point towards it; conversely, a negative ion attracts water molecules so that the positively charged hydrogen atoms point towards it. These effects tend both to disrupt the surrounding clusters and to immobilize the more freely moving water molecules; also a layer of water molecules tends to form on the surface of each dissolved ion. The effects are more pronounced for highly charged ions than for ions of lower charge. The aluminium ion Al^{3+}, for example, attaches a layer of six water molecules to itself very firmly and several other layers rather less firmly. The potassium ion, having only one positive charge, interacts less strongly and probably only goes so far as to cause some disruption of the adjacent water clusters without actually acquiring a firmly attached layer of molecules. The size of the ion is also important. The lithium ion, Li^+, although having the same charge as potassium, is very much smaller. It can therefore approach water molecules more closely and the consequently stronger coulombic forces give rise to the attachment of probably four molecules. This difference in behaviour between potassium and lithium is exemplified by the fact that lithium salts crystallize with water of crystallization whereas potassium salts form anhydrous crystals.
The sum of all the interactions taking place between ions and water molecules in solution is known as the *hydration of ions*. Ions to which molecules of water have been attached more or less firmly are said to be *hydrated*. Small highly charged ions tend to be strongly hydrated, while larger and less highly charged ions tend to be less hydrated, if at all. However, there is in all cases an

These complex interactions between ions and water molecules are accompanied by corresponding energy changes. Taken together with the effect of the high dielectric constant they provide sufficient energy to allow the strong forces holding the crystal together to be overcome so that the salt goes into solution.

appreciable *hydration effect* which has an important bearing on the properties of ions in solution.
When we study the behaviour of ions in solvents other than water we use the more general term *solvation* to describe the interactions taking place. ..."

Selley [[27] has ideas similar to the above:

"... The manner and extent of hydration of aqueous ions are not properly understood, and only recently have techniques such as the effect of high pressure on conductivity begun to provide answers. There is little doubt, though, that the hydration arises from electrostatic attraction between the ion and either the partly negative O or the positive H atoms of appropriately oriented H_2O molecules. The energy of hydration (and hence the number of molecules held) is a function of the charge density on the ion (which increases with smaller size and higher charge). ..."

On the other hand, Antropov [28] says:

"... According to the views widely accepted at present and based on the works of Kablukov, the energy bringing about the rupture of bonds in the molecules of an electrolyte is produced by interactions between its ions and solvent particles (when water is the solvent, the process is known as *hydration*). This energy is equal to the change of the Gibbs free energy taking place during the reactions

$$M^{z+} + xH_2O = M(H_2O)_x^{z+}$$

and

$$A^{z-} + yH_2O = A(H_2O)_y^{z-}$$
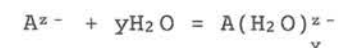
which give rise to hydrated ions. Similar processes are also found to occur in nonaqueous solutions, but leading to the formation of solvated ions (the process known as *solvation*). The energy effects of these two types of reactions are known as the *hydration energy* $-\Delta G_h = U_h$ and the *solvation energy* $-\Delta G_s = U_s$, and the corresponding thermal effects as the *heat of hydration* $\Delta H_h = \overline{Q}_h$ and the *heat of solvation* $-\Delta H_s = \overline{Q}_s$ (as suggested by Fajans). ..."

Burgess' proposal [29] in 1978 is very similar to Frank and Wen's [12]; he considers four regions described as follows:

"... (A) The primary solvation shell of the cation. This contains water molecules, often six in number, directly interacting or bonding with the cation.
(B) A region of secondary solvation. Here the cation has an influence over the water molecules, and its

electron-withdrawing effect on the primary waters of hydration encourages them to hydrogenbond to secondary waters of hydration. The volume of this secondary shell varies greatly with the nature of the cation, being large for small ions of high charge and small or negligible for large monopositive cations.

(C) A disordered region, or 'fault zone', necessarily separating the ordered region of (A) and (B) from the differently ordered region (D). Again the extent of this region depends on the properties of the metal ion involved.

(D) Bulk solvent.

This picture only applies fully in very dilute solutions, where the mole ratio water: cations is large enough to provide sufficient water molecules so as to surround each cation to the extent indicated. ...

... Phrased in terms of structural properties of solvents, (A) and (B) are regions where the ion makes its presence felt in a structure-making capacity, region (C) in a structure-breaking capacity. Ions with a low charge density (small charge, low radius) will have a relatively small structure-making region and act as net structure breakers, whereas for ions of high charge density (large charge, small radius) structure-forming will dominate. For example, region (C) is thought to be practically absent from the surroundings of the very small Li$^+$ cation. ...
... The concept of structure-breaking is an alternative description of so-called **negative hydration** [14]. ...
... The most important point to make at this stage with respect to cation solvation numbers is that they vary according to the experimental method used in their estimation. For cations at which solvent exchange is sufficiently slow, n.m.r. spectroscopy gives the number of solvent molecules in the primary coordination shell, region (A) ... On the other hand, methods of estimation based on the motion of solvated ions through the liquid give an indication of the number of solvent molecules which actually move with the ion. Such estimates include some secondary solvent molecules, region (B), as well as those adjacent to the ion in the primary solvation shell. ..."

We should note that with this last paragraph Burgess [29] has a different opinion from Bell's [16] as previously cited. In fact, Bell [16] considers that we can obtain values of the parameters "h" concerning only primary solvation from diffusion coefficients, one method of determining hydration numbers.

Recently, 1983, Impey [30] says:

"... Our present understanding of the changes which occur is strongly influenced by the work of Frank and Gurney [12, 13, 31] ..."
"...The picture that we have sketched is familiar one of a hydrated ion; the number of molecules which

contribute to the hydration is called the hydration number of the ion. Much experimental effort has been devoted to determining the hydration numbers of different ions. ..."
"... The most striking feature of the data that they compile is the fact that different experimental techniques can lead to vastly different estimates of the hydration number. ... A number of factors contribute to this uncertainty, including the difficulty of partitioning the hydration number for a salt into separate contributions from the cation and anion. However, the main reason for the wide spread in results is undoubtedly the fact that different types of measurements are sensitive to ion-solvent correlations over different ranges of both distance and time. ..."
"... For the concept of hydration number to be useful, a definition at the microscopic level is required. Following Bockris and Reddy [15], we shall interpret the hydration number of the ion as being the number of water molecules which are bound to the ion for times sufficiently long that they participate in the diffusive motion of the ion. Such a quantity could appropriately be termed a dynamic hydration number. In a simple theory, the ion and its hydration shell may be treated a single kinetic entity. One of the main objects of the present paper is to propose an examine the usefulness of a dynamic hydration number defined in terms of the residence time of water molecules in the region close to the ion.

It is also possible to speak of a coordination number, equal to the mean number of water molecules in the first coordination shell of the ion. The definition of the later is itself arbitrary, but once a convention has been chosen the coordination number is unambiguously specified. The terms coordination and hydration are sometimes used interchangeably, but for our purposes it is precisely the difference between them which is of interest. The coordination number is determined solely by the static structure of the solution and is measurable, in principle, by X-ray and neutron diffraction methods. The concept of hydration number is a wider one, since it involves the adoption of a suitable time scale. ..."

Horvath [32] discusses Samoilov's and Frank and Wen's models (among others) saying that both have limitations, particularly if a quantitative perspective of the nature of electrolyte solutions is pretended. Concerning Frank and Wen's model he says:

"... This model gives a qualitative picture of the ion-water interaction. However, it does not provide arrangements for the molecules in the regions discussed. ..."

Concerning Samoilov's model, Horvath [32] says:

"... In this model the interaction of the ion with the closest water molecules is considered. It does not, however, provide a definite picture for the structural arrangement for the layers around an ion. ..."

Later, he [32] adds:

"... Statistical thermodynamics has been used widely for obtaining quantitative descriptions of the ion - molecule interaction model. ..."
"... The different proposals for developing a model have not been consistent with regard to the distinction between the solvation and the coordination number (Bockris at al., 1970; Bockris and Saluja, 1972). The definitions are as follows:

i) The solvation (or hydration) number is described by the number of water molecules which remain associated with the ion during its movement through the solution.
ii) The coordination number is the total number of water molecules which are in contact with the ion.

Usually the solvation number will be less than the coordination number. In the case of small ions the solvation and coordination numbers are the same. With large monovalent ions, the solvation number tends to be zero.

As pointed out earlier, one of the important aspects of the existing models for the structure of aqueous electrolyte solutions is to decide how many water molecules are in the solvation and in the coordination shells. The lack of inadequacy of the techniques used for the establishment of the number of water molecules surrounding the ion contributed to be shortcomings of several models. ..."

Horvath's [32] conclusion is:

"... It is difficult to expect to find and understand the ion-water molecule interaction until the structure of liquid water becomes clear and fully understood. ..."

Ahluwalia [33], comments the applicability of Frank and Wen's model for the understanding of the structure of solutions, comparing with other models, namely Friedman and Krishnan one:

"...Friedman and Krishnan [34] from their thermodynamic studies, conclude that the electrostatic model (which considers solvent as a dielectric continuum) is inadequate to describe ionic solutions. They have proposed a model for aqueous ionic solutions, based on ideas given by Frank and Evans [31], Gurney [13], and Samoilov [1]. They assume that around each solute particle X^z (Z = charge of the ion), there is a region termed as co-sphere, having the thickness of one solvent molecule in which the solvent properties are affected by the presence of the solute and these effects are characterised by the thermodynamics of the process,

n[solvent(pure bulk liquid)]--n[solvent in co-sphere state next to X^z]

where, n = number of solvent molecules in the co-sphere.
While the Frank and Wen [12] model and more recent, Ben-Naim-Stillinger [35] model of ionic solutions are rather qualitative and are supported by the considerations of kinetic properties or the way the solutions scatter X-rays or neutrons [36], the Friedman-Krishnan model emphasises on the contributions of the various co-sphere states to the thermodynamic properties of solutions.
Computer simulation studies [37, 38] on aqueous electrolyte solutions have confirmed the presence of two types of hydration shells, *viz.* the inner hydration shell with a well defined hydration number (ions with low charge densities are exceptions) and outer hydration shell where water-water correlation depicts a decrease in "structure". ..."

Chialvo [39] gives the following contribution:

"The behavior of water molecules around an ion in solution may be described by the changes produced in their spatial distribution. In the closest region around simple ionic species, the solvent exhibits a more ordered structure. This order decreases with an increasing distance to the ion, the mobility of water molecules consequently increasing. A dynamic equilibrium between both free and bound solvent molecules is thus established. This description ignores the presence of other species originated by ion-ion interactions such as ion-pairing, dissociation equilibria, etc. Consequently, this model based on a mechanism of consecutive hydration equilibria is restricted to the case of simple, uni-univalent, unassociated electrolytes having low to moderate concentrations. ..."

Recently, 1988, Wright [40] does not follow Samoilov's considerations when he says:

"... A solvation sphere could be defined as a sphere of water molecules which are closely bound to the ion and move around with the ion as **one single moving** entity, with these solvent molecules having lost their own independent translational motion. The moving ion is thus larger than the bare ion as measured by the crystallographic radius. The bound water molecules contribute to the size of the ion and are very much affected by the ion. Molecules outside the solvation sphere may nonetheless be affected by the ion, with no real sharp cut-off. ..."

However, he notes the following:

"... We must be very careful to distinguish between:

regions of the solvent where solvent molecules are actually bound to the ion
and
regions of the solvent which are affected by the ion but are not bound to it.
This distinction is vitally important."

It is interesting that Wright [40] presents the solvation number similarly to Bockris [3, 15]:

"... The interactions giving rise to solvation are believed to be typically ion-dipole interactions. ..."

Recently Ohtaki and Radnai [41] conclude:

"... In the time from 1930s to the 1960s, various classical methods have been applied to investigate these problems. However, confusion in understandings of the structure of hydrated ions has been noticed in this period because of scattered data obtained by different methods and the lack of information of static and dynamic properties of water molecules coordinated to ions. When new methods were applied to the field of solution chemistry beginning in the 1970s, which became possible owing to the development of modern electronics and high-speed electronic computers, a steep increase in publication of interesting papers was seen in studies on the structures of hydrated ions, dynamics of coordinated water molecules, and interaction energetics of ions with water molecules . ..."
"... The concept of the structure of hydrated ions largely depend on the methods of observation. We may classify the structure of hydrated ions into three categories depending on the methods of investigations as follows:

(1) Static structure, in which the structure is discussed on the time and space averaged ion-water interactions. Results obtained by X-ray and neutron diffraction methods are included in this category.

(2) Structure discussed on the basis of dynamic properties of coordinated water molecules. Results obtained by NMR measurements may be the typical case.

(3) Energetic considerations lead to the discrimination of strongly combined water molecules with ions from loosely interacting water molecules to ions. Spectroscopic investigations, including frequency measurements by Raman and IR spectroscopies and thermodynamic studies on ionic hydration give us information on water molecules strongly coordinated to ions. Information on water molecules weakly interacting to ions is always ambiguous. ... It is obvious that the structure of hydrated ions discussed in terms of static and dynamic properties of water molecules coordinated also depends on interaction energies between ions and water molecules. Therefore, the classifications of the concept of ionic hydration is conventional. ..."

Conclusions

The concept of ionic solvation (or hydration) deals with all the interactions between the solvent molecules (frequently water) and a dissolved ion, but the nature of those interactions is not yet fully known. A quantitative description of that concept may be based in the hydration number [3] or in the ΔE parameter [14], both with limitations as we previously indicated.

From the interpretation of our measurements in diffusion in electrolyte solutions (e.g. [42-46]) we tend to conclude that Wright's approach [40] presents the best concept of ionic solvation: "... sphere of water molecules which are closely bound to the ion and move around with the ion as one single moving entity, with these solvent molecules having lost their own independent translational motion. ..."

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