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Ionic Solvation in Aqueous and Nonaqueous Solutions

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Summary. The history of studies on ionic solvation is briefly reviewed, and structural and dynamic properties of solvated ions in aqueous and nonaqueous solutions are discussed. An emphasis is placed on ionic solvation in nonaqueous mixed solvents in which preferential solvation of ions takes place. A new parameter for expressing the degree of preferential solvation of an ion is proposed.

Keywords. Ionic solvation; Nonaqueous solutions; Mixed solvents; Preferential solvation; Preferential solvation quotient.

Introduction

All ions and molecules in solution are more or less solvated, and thus solvated ions are the most fundamental species for ionic reactions in solution. A number of monographs have been published in recent years on this subject [1–8], and two important reviews have appeared recently [9, 10]. Two review books have been published in Japanese [11, 12].

Although many electrolytes dissolve in water, they are usually hardly soluble in nonaqueous solvents. Some organic solvents with relatively high dielectric constants or large donor and acceptor properties can be good solvents for electrolytes. In mixed solvents, ions are preferentially solvated by one solvent compared to the other. Such preferential solvation has been phenomenologically observed in many experiments such as conductivity, enthalpy, viscosity measurements, *etc*. However, no quantitative discussion has been undertaken for describing the degree of preferential solvation, because the solvent composition in the solvation sphere of ions can hardly be explored by experiments. Development of X-ray diffraction techniques for solution allows to see individual solvent molecules in the solvation shell, and accumulation of data for preferential solvation of ions in mixed solvents has allowed to discuss to some extent causes of preference of solvents recently. In this article, ionic hydration from the past to the present is briefly reviewed from static as well as dynamic points of view, and the results of ionic solvation in neat and mixed nonaqueous solvents are

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summarized. Experimental results so far reported are rather limited for solvation of ions in nonaqueous solvents and very limited in mixed solvents. Nevertheless, it may be very interesting and useful to discuss preferential solvation phenomena in a quantitative way. A special emphasis is placed on the introduction of a parameter representing the degree of preferential solvation which relates to the *Gibbs* energies of solvation of ions in two solvents. Exceptions from the representation of preferential solvation in terms of solvation energies of an ion in individual solvents in a mixture are discussed by taking into account specific ion-solvent and solvent-solvent interactions and steric effects of bulkiness of solvent molecules.

Solution Chemistry in the Time of *Arrhenius*

More than one century has passed since the publication of the Dissociation Theory of Electrolytes by *Arrhenius* [13]. Before *Arrhenius*, it was believed that electrolytes did not dissociate into ions in water until current was passed. An electric field produced between two electrodes could separate cations and anions in the electrolytes according to the considerations of *Clausius*. *Faraday*'s study on electrolysis in 1833 and the law of independent migration of ions proposed by *Kohlrausch* in 1855 were explained on the basis of this concept. The theory of ionic dissociation proposed by *Arrhenius* in 1887, in which he stated that electrolytes spontaneously separate into positive and negative ions in water against the electrostatic attraction between the ions, was not well accepted by the majority of scientists, and even *Arrhenius* himself could not explain the reason why positive and negative ions could separate against the *Coulomb* attraction between them. The source of the energy for separation of ions was unknown at that time.

Structural studies of water on the molecular level have been examined at the beginning of 1930 [14–16] which gave experimental evidence to the theoretical study of *Bernal* and *Fowler* [17]. However, elucidation of ion-water interactions in solution at the molecular level came much later.

Development of Solution Chemistry until 1957

At the beginning of the 20th century, many chemists studied solution chemistry (of course the term solution chemistry was not yet created, and their studies were recognized as those of physical chemistry), and *van't Hoff, Kohlrausch, Arrhenius*, and *Ostwald* are but some examples. Most of them employed methods of electrochemistry, and their discussions mostly concerned the static point of view. Some investigations based on dynamic properties of ions such as elecrtroconductivities and viscosities of solution had also been carried out in the period of 1900–1920. Electrochemistry was very useful for studies on solution chemistry until 1930–1940.

An important study was published by *Debye* and *Hückel* in 1923 [18]. Their theory of ionic activities in solution played a key role for explaining non-ideality of ion-ion interactions. The size of ions introduced by them as 'the distance of closest approach', which was later changed to 'ion size parameter', suggested that the sizes of ions in solution must differ from that of the naked ones due to ion-solvent interactions. The *Debye-Hückel* theory contributed to the elucidation of not only static properties of ionic activities but also dynamic ones of ionic mobilities and diffusion coefficients. The theory of ion-pair formation by *N. Bjerrum* [19] was induced by the *Debye-Hückel* theory. *Born*'s theory [20] for ionic solvation was welcom by many physical chemists due to its good fitting to experimental results in water and in water-like alcohols and its simple form, although the defect of the *Born* theory was pointed out when enthalpies and entropies of ionic solvation were measured and other nonaqueous solvents than alcohols having iso-dielectric constants were used.

However, in all theories solvents were assumed to be a dielectric continuum with specific properties, and no concept on a molecular level had been introduced. The contradiction between ionic sizes reduced with respect to the ion size parameters predicted by the *Debye-Hückel* theory or *Stokes* radii of ions obtained from the mobility of ions in solution and the radii of naked ions for some alkali and halide ions could not be solved until *Frank-Wen* [21] and *Samoilov* [22] proposed their theories for structure-making and structure breaking of ions and negative hydration, respectively, at the *Faraday Discussion* in 1957. Then, ionic solvation was discussed by taking into consideration the structure of solvents, especially the water structure for ionic hydration.

Ionic Hydration

The time from 1930 to 1940 may be called the first golden period of solution chemistry. In this period, various classical methodologies had been applied in studies of ionic hydration. Since electrolyte solutions contain, at least, two ionic components, *i.e.* cations and anions, and thermodynamic properties of both ions are not separately measured by experiments, some assumptions have to be introduced when measured properties are to be separated into cationic and anionic ones; otherwise, hydration numbers of individual ions are not determinable.

The nuclear magnetic resonance (NMR) method is very useful for probing the hydration number of ions, and many authors have reported the hydration numbers of various ions determined this way since 1960. However, without complicated corrections, this method will only determine the number of water molecules strongly bound to ions, *i.e.* those with substitution reaction rate constants below 10^9 s^{-1}. Most halide ions have much higher exchange rate constants, and thus their hydration number was assumed to be practically zero. Although this assumption does not introduce any serious errors for the determination of hydration numbers of cations, it seemed strange to see that most anions had no hydrated water molecules in solution. Moreover, this assumption is contradictory to the theories of *Frank-Wen* and *Samoilov*.

Solution X-ray (XD) and neutron diffraction (ND) methods and the extended X-ray absorption fine structure (EXAFS) method can overcome this difficulty and provide hydration numbers of individual ions without any assumption. The solution X-ray diffraction method, which is much easier to handle than the neutron diffraction method, has been used quite widely for the determination of hydration numbers of various ions. The method can also determine the lengths of ion-oxygen bonds in the hydrated species. By ND we can obtain the same structural parameters as well as the tilt angle of water molecules around the ions by knowing ion-oxygen and ion-proton distances in the solvation shell. In these methods, different from others previously employed for the determination of hydration numbers, the number of water molecules around an ion is found from the analysis of radial distribution functions, independent of the strength of the ion-water bonds. An ion with a large ionic size is determined to have a large hydration number, and the reverse is true for small ions. Therefore, the number of water molecules in the first solvation shell of a small ion such as Li^+ or Be^{2+} is low (four in these cases), but a large ion such as caesium, which is a typical structure breaker and weakly combined with water molecules, is found to have a large number of water molecules around the ion (about eight). It should be noted that the hydration numbers determined by the diffraction methods represent the time- and space-averaged number of water molecules around ions, as are those found by any other method, and distribution of hydration numbers of ions in the same solution and fluctuation of the number with time are not experimentally determinable at present. Computer simulations such as molecular dynamics (MD) simulations have to be used to observe molecular arrangements and movements of hydrated ions in more detail.

The methods employed for the determination of solvation numbers of ions are summarized in Table 1, with comments upon what they are measuring. The solvation numbers determined by most thermodynamic methods are rather ambiguously defined. By these methods, not only solvent molecules in the first solvation shell but also those in the second or even in further shells are frequently detected.

Some examples for the way of estimation of hydration numbers of ions are illustrated below:

1) The mean activity coefficients obtained from the *Debey-Hückel* theory may be divided into separate activity coefficients of cations and anions. Both include ion-size parameters ($\mathring{a}$) which reflect the sizes of their hydrated ions in aqueous solution, and thus the thickness of the hydration sphere can be estimated from the values of the ion-size parameter and the ionic radius of the naked ions. However, it is obvious that from these data the number of water molecules in the hydration shell cannot be determined because the volume of one water molecule in the hydration sphere cannot be evaluated. The ion-size parameter is a parameter evaluated under the assumption of a continuum of the bulk water, which is far from reality.
2) The density of aqueous electrolyte solutions may be explained in terms of bulk water of normal density and high-density water in the solvation sphere. However, the density of the solvation sphere may gradually change with the distance from the center of an ion; the first solvation shell has the highest density, and then the density should decrease in the next shells. The change in the densities in these spheres and the mass of the electrolyte cannot be evaluated.
3) The hydration numbers of some ions have been evaluated from the hydration entropies of the ions under the assumption that the hydration entropy per molecule equals that of freezing. Of course, this assumption is too naive.
4) The compressibility of solutions has been divided into two terms: compressible bulk water and incompressible hydrated water. The two-state assumption is too simple, and water phases of various compressibilities may exist from the first hydration shell to the bulk.

Table 1. Methods employed for studies on ionic hydration

Method	Region
Diffraction (X-ray, neutron)	Mainly the 1st shell; when the isomorphous substitution method is applied, the 2nd shall can be studied
X-ray absorption (EXAFS, XANES)	1st shell
Electron diffraction	1st shell of ions in quickly frozen solution (solid)
Computer simulations (Molecular dynamics, Monte Carlo)	1st and 2nd shells
Spectroscopy	
Visible, ultraviolet, infrared	1st shell
Raman	1st shell
NMR (chemical shift, line broadening)	1st shell
Mössbauer	1st shell
Thermodynamics	
Enthalpy and entropy of hydration	Not clear
Compressibility	Mainly the 1st shell
Activity	Mainly the 1st shell, but not clear
Vapor pressure, boiling and melting points	Mainly the 1st shell, but not clear
Density	Not clear
Solubility, salting out	Mainly the 1st shell, but not clear
Mobilities	
Transport number	Not clear
Mobility, diffusion coefficient	Not clear
Reaction kinetics	
Isotope dilution	1st shell
NMR	1st shell

These are just examples, and one can easily consider how simple and brave assumptions have been employed in studies of hydration numbers of ions in the past.

NMR measurements introduced in the sixties of the last century have also been employed in the study of ionic hydration, the method being first used for the determination of the hydration structure (static structure) and then for investigation of the dynamic behavior of hydrated water molecules. The NMR method is much advantageous compared with thermodynamic methods, because more direct information is obtainable for the number of water molecules which are practically fixed to ions, and the method allows to use ^{2}H and ^{17}O instead of ^{1}H and ^{16}O in water. Since the frequency of the magnetic field applied to a magnet in the NMR apparatus is in the order of 10^{8} Hz, the NMR method can be used without special correction for solutions of Cr^{3+} and Al^{3+} whose rates of the solvent exchange reaction are very slow. The hydration numbers of ions in solution, the exchange rate constant of which is in the order of 10^{3}–10^{7} s^{-1}, may be determined rather safely with suitable corrections. However, for ions with much faster solvent exchange rates, the NMR method has difficulties in correctly determining the hydration number of ions. Thus, the hydration number of anions is usually assumed to be one to zero, which is quite ridiculous. If the hydration number of anions were zero, an electrolyte were not soluble in water.

The most reasonable values for hydration numbers of ions have been determined by XD. Early works by XD are sometimes rather doubtful, because investigators did not well understand chemical equilibria in solution, and sometimes they neglected ion-pair and complex formation reactions between cations and anions and hydrolysis of cations in a neutral solution. Most of reliable results for the hydration numbers of ions are reported from the beginning of seventies.

In solution XD measurements, the hydration structure of cations and anions can be obtained independently and without any assumption, because most cations and anions have different ionic sizes which produce peaks at different positions in the radial distribution curve of a solution. In XD measurements, the hydration number of an ion is defined to be the number of water (solvent) molecules around an ion, independent of the bond strength between ion and hydrated water molecules. Therefore, the number of hydrated water molecules determined by the XD method, as well as by ND and EXAFS, is different from that evaluated by thermodynamic and other methods previously employed. If the attention is focused on the number of water molecules in the first hydration shell, the hydration number of a caesium ion is larger than that of a lithium ion due to the large surface area of the former ion with respect to the latter. The bond strength of hydrated water molecules to the central ions is given in terms of the temperature factor of the ion-water pair.

The orientation of water molecules around an ion cannot be determined by XD; only ND is capable to evaluate the structure parameters on the orientation of water molecules in the hydration shell, although sometimes experimentally obtained structural parameters do not coincide well with the results found by molecular dynamics simulations, which usually provide a reasonable agreement with results from XD for other structural properties of hydrated ions.

The ND method has a great advantage compared with XD and EXAFS measurements, because the former can use isotopes with different neutron scattering cross sections. The isotopic substitution method in ND measurements can provide very detailed structural information of hydrated ions when experiments are carried out very precisely and accurately. The reliability of ND data is sometimes lower than that of XD, because the scatter of measured neutron intensities at each point is much larger than that of XD. The *Jahn-Teller* distorted structure of the hexahydrated copper(II) ion in water was revealed by XD [23], but by ND the elongated Cu–OH_2 bonds at the axial position were not well seen [24]. The neutron scattering experiments are more enthusiastically employed for studies of dynamic properties of hydrogen atoms and other light atoms in molecules by using the quasi-elastic neutron scattering (QENS) technique.

The Extended X-ray Absorption Fine Structure (EXAFS) method is now often used for the determination of structures of hydrated ions and complex species in solution. The method is widely used for complicated systems which can hardly be studies by XD and ND because of its high selectivity of atoms and high sensitivity. Many biological samples have been investigated by this method. However, EXAFS can detect almost only the first neighbor atoms, and thus the structure of the second coordination shell and other long range interatomic interactions can hardly be discussed by this method. The X-ray Absorption Near Edge Structure (XANES) method is also widely employed to study the structure of complex species and the electronic state of the X-ray absorbing atom.

Computer Simulations Applied to Ionic Solvation

In the last decades, computer simulations have been rapidly developed, inspired by the progress of high-speed electronic computers. Computer simulations applied to solution chemistry may be classified into three groups: 1) Molecular Mechanics (MM), 2) Monte Carlo (MC), and 3) Molecular Dynamics (MD) simulations.

The first one is usually used for an estimation of the most stable configuration of a given molecule, and solute-solvent interactions are not well taken into consideration. However, for molecules containing many atoms and having a complicated form (mostly organic molecules), application of MM may be useful for estimating the most stable molecular form of an isolated molecule, which may not be changed in solution. Since MM mostly focuses its attention on the atomic configuration in a molecule and on the search for the lowest atom-atom interaction energy of a molecule, it is not convenient to discuss the structure of liquids and solutions containing a large number of atoms and molecules. Moreover, MM does not give clear information for the dynamic behavior of liquids and solutions.

Monte Carlo simulations have widely been used for discussing atomic arrangements in solution of lowest energy. However, MC calculations intend to reproduce molecular arrangements of the lowest energy in a system by changing atomic positions step by step with the help randomly generated numbers. Moreover, since the change in the molecular arrangement is time-independent, it is not possible to discuss dynamic properties of liquids and solutions.

Compared with the above two methods, MD simulations are much more useful for elucidating both static and dynamic properties of liquids and solutions. Combination of Molecular Orbital (MO) calculations for relatively small ensembles of the central ions and solvent molecules around the ion with MD calculations for the whole molecular system in a unit cell may provide a new way for structural studies on solvated ions and molecules and for the investigation of dynamic properties of the solvated species in solution.

The reliability of results obtained by computer simulations must be checked by comparing them with experimental results. For static properties, *i.e.* the structure of solutions, results from XD and ND methods are usually employed. For dynamic properties, *i.e.* the time of residence of solvent molecules in the solvation shell of an ion and rates of solvent exchange reactions, mostly NMR data are quoted. However, the time scale of MD simulations is too short (ps to ns time scale) compared with the time scale of the residential time of solvent molecules around an ion and the rate of solvent exchange reaction of most ions (usually 10^{-10} s to μs time scale, or even ms), and thus, it is not easy to certify the results obtained by MD simulation on the basis of experimental results.

Structure of Hydrated Ions

A sufficient accumulation of data for the structure and dynamic properties of hydrated ions has been seen in the past decades since 1960. The hydration structure of most single atomic cations and anions in water has been determined by MD, ND, and EXAFS methods. Orientation of water molecules in the solvation shells is not well elucidated, however. Although ND can determine the distances between the central ion and hydrogen atoms and between the ion and the oxygen atom of a solvated water molecule from which the tilt angle of the water molecule can be estimated, only a limited number of data are available, and they are not always in good agreement with the results found from MD simulations. On the other hand, dynamic properties of hydrated water molecules have been compiled with insufficient accuracy due to experimental difficulties. Rates of exchange of hydrated water molecules in solution have been experimentally determined after the works by *Eigen et al.* [25]. The development of the NMR method in measurements of dynamic properties of solvated ions accelerated the accumulation of experimental results. The data have been summarized in many books [1–8, 11, 12] and reviews [9, 10], but some of the typical results are illustrated in the following sections.

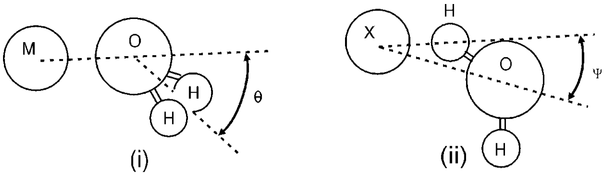
The hydration numbers and distances between central ions and oxygen atoms in the hydrated water molecules have been determined by NMR, XD, ND, and EXAFS methods. The tilt angles of hydrated water molecules around some metal ions which have suitable isotopes have been found by ND, although discrepancies of the experimental results by ND and MD have been observed in some cases, probably due to large scattering of experimental data in ND measurements, and thus the reliability of the results for the orientation of hydrated water molecules may be lower than that for the hydration numbers and bond distances of hydrated ions.

Table 2 summarizes selected results among various experimental results reported [10]. Cases with more than one entry show that it cannot be concluded which result is more reliable from the literature (*e.g.* Li^+ and NH_4^+) or that different results have been found from different methods (for example, by XD, ND, and EXAFS for H^+, Ca^{2+}, Fe^{2+}, Ni^{2+}, Cr^{3+}, *etc.*).

Generally speaking, results by NMR agree with those by the diffraction methods (XD, ND, EXAFS). However, if we define the hydration number to be the number of water molecules in the nearest neighbor of an ion, the results obtained by the diffraction methods are more reliable than those by NMR, because the NMR method cannot well measure the number of water molecules moving fast within less than *ca.* 10^{-9} s. The hydration numbers of most anions are given to be one to zero by NMR. The results found by XD, ND, and EXAFS usually agree with those drawn on the basis of coordination chemistry. However, the hydration numbers found for alkali and alkali earth metal ions are not always in good agreement with the results derived by *Frank-Wen*'s and *Samoilov*'s considerations, because the hydrated water molecules determined by the diffraction methods do not always imply water molecules strongly combined with the central ions. On the other hand, NMR measurements detect only water molecules strongly combined with ions and moving slowly with respect to the NMR time scale.

Non-integer hydration numbers are obtained for some ions. Although no clear explanation has been given for such non-integer hydration numbers found by NMR, non-integer hydration numbers obtained by the diffraction methods, including EXAFS, have been well illustrated in terms of (*i*) experimental errors, (*ii*) the use of symmetrical *Gaussian* functions at the analysis of radial distribution functions, (*iii*) an ion having, at least, two different hydration numbers, and (*iv*) an ion having a

Table 2. Selected values of hydration numbers and bond angles of ion-water interactions in the first hydration shell of cations and anions determined by NMR, X-ray, neutron diffraction, and EXAFS[a]



Orientation of water molecule: (*i*) M = cation, (*ii*) X = anion

	NMR					X-Ray, neutron diffraction, EXAFS				
Ion	Hydration number n	Nucleus	T/°C	Method	Ref.	Hydration number n	Bond length $(r_{M\text{–}O}, r_{X\text{–}O})$/pm	Bond angle (θ, Ψ)/°	Method	Ref.
H^+	2.5	^1H	broad T	cs	[1]	3 1	244 290		X	[13]
						4	288	$\theta = 0$	N	[14]
Li^+	3.0	^1H	broad T	cs	[1]	3.3	195	$\theta = 52$	N	[15]
						5.5	195	$\theta = 40$	N	[15]
Na^+	3.5	^1H	broad T	cs	[1]	6	244–248		X	[16]
K^+	3.0	^1H	broad T	cs	[1]	6	280		X	[17]
Rb^+	3.5	^1H	broad T	cs	[1]					
Cs^+	3.0				[2]	8	295	$\theta = 54.75$	N	[18]
NH_4^+						4	280–288		X	[19]
						8	304		X	[20]
Ag^+						4	243		X	[21]
Be^{2+}	4	^1H	−20–100	pa	[3]	4	167		X	[22]
Mg^{2+}	6	^1H	−67–−90	pa	[4]	6	212		X	[23]
Ca^{2+}	6.0	^1H	broad T	cs	[1]	6	244		X	[24]
						5.5	240	$\theta = 51$	N	[25]
						8	246		E,X	[56]
Sr^{2+}	5.0	^1H	−20–100	pa	[3]	8	264		X	[26]
Ba^{2+}	5.7	^1H	−20–100	pa	[3]	9.5	290		X	[27]
Cr^{2+}						4^b	208		E	[28]
Mn^{2+}						6	220		X	[29]
Fe^{2+}	5.6–5.8	^1H	−40–−80	cs	[5]	6	212		X	[29]
						6	213	$\theta = 32$	N	[30]
Co^{2+}	5.9	^1H	−38–−63.7	pa	[6]	6	208		X	[29]
Ni^{2+}	6	^{17}O	< 127	cs	[7]	6	204		X	[29]
						5.8	205	$\theta = 30$	N	[31]
Cu^{2+}						4 2	194 238		X	[29]
Zn^{2+}	5.9–6.4	^1H	−120	cs	[4]	6	204		X	[29]
Cd^{2+}	4.6	^1H	−20–100	pa	[3]	6	231		X	[32]
Hg^{2+}	4.9	^1H	−20–100	pa	[3]	6	241		X	[33]
Sn^{2+}						3.6	234		X	[34]
Pb^{2+}	5.7	^1H	−20–100	pa	[3]					
Al^{3+}	6.0	^1H	−35–−52	pa	[8]	6	187		X	[35]

(*contd.*)

Table 2 (*continued*)

Sc^{3+}	5.1	^{1}H		pa	[8]	6	187		X	[35]
Cr^{3+}	6.0	^{17}O	20	pa	[9]	6	199.7		X	[36]
						6	197		X	[57]
						5	195	$\theta = 36$	N	[37]
Fe^{3+}						6	201	$\theta = 41$	N	[38]
Ga^{3+}	5.89	^{17}O	35	pa	[10]	6	196		X	[57]
Y^{3+}						8	236		X	[39]
Rh^{3+}						6	206		X	[40]
In^{3+}	5.8–6.0	^{1}H	-89–-99	pa	[11]	6	215		X	[41]
Ti^{3+}						5	223.6		X	[42]
Bi^{3+}						8	241		X	[58]
La^{3+}	6.0–6.4	^{1}H	-105–-120	cs	[5]	9.1	258		X	[43]
						6 3	252 264		X	[59]
Ce^{3+}	4.5–5.5	^{1}H	-110	cs	[5]					
Pr^{3+}						9.2	254		X	[43]
Nd^{3+}						8.9	251		X	[43]
Sm^{3+}						8.8	247		X	[44]
Eu^{3+}						8.3	245		X	[44]
Gd^{3+}	8 or 9	^{1}H			[12]	8.0	237		X	[45]
Tb^{3+}						8.0	240		X	[39]
Dy^{3+}						7.9	239		N	[46]
Er^{3+}						8.0	236		X	[39]
Tm^{3+}						8	233	$\theta = 12$	N	[47]
Yb^{3+}						8	233	$\theta = 12$	N	[47]
Lu^{3+}						8.0	234		X	[48]
Sn^{4+}	6.0	^{1}H		pa	[8]	8.0	234		X	[48]
Th^{4+}	9.1	^{1}H		pa	[8]	7.9–8.1	248.6		X	[49]
						10	245		X	[60]
U^{4+}						7.9	250		X	[50]
						10	242		X	[60]
F^{-}						6	269		X	[19]
Cl^{-}						5.3–6.2	222–226	$\Psi = 0$–6	N	[51]
Br^{-}						8	320		X	[52]
I^{-}						8.3	358		X	[53]
NO$_3^{-}$						7.2	340^{c}		X	[21]
ClO$_4^{-}$						8	380^{c}		X	[54]
SO$_4^{2-}$						8.2	379		X	[55]

^{a}broad *T*: values obtained from temperature *T* and concentration *c* dependencies of chemical shifts over a broad range of *T* and *c*; cs: determined from chemical shifts; pa: determined from peak area; X: X-ray diffraction; N: neutron diffraction; E: EXAFS; ^{b}Cr^{2+}$-$OH$_2$ bonds elongated along the axis were not observed; ^{c}$X-$OH$_2$ distance beyond the O atom directly combined with X

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(Table 2 ref. notes continued)
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distribution in hydration numbers over a relatively wide range of numbers. Evidence for the distribution of hydration numbers around an ion has been obtained from MD for many ions of large ionic size and low electronic charge, such as alkaline metal ions and halide ions. The results for many anions belong to case (*iv*), whereas lanthanide ions are believed to belong to case (*iii*).

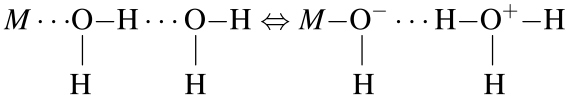
The observed bond length between an ion and a water molecule is close to the sum of the ionic radius reported in the literature and the *van der Waals* radius of a water molecule (140 pm). According to ND results, water molecules around an ion are not directed towards the dipole of the water molecule but tilt by an angle θ. An explanation of the tilt angle in terms of the sp^3 structure of a water molecule is no more acceptable, because it is not believed that a water molecule has an sp^3 electronic configuration of the ST2 type [26], but two positive charge at the hydrogen atoms and one negative charge at a point very close to the central oxygen atom, and no electronic orbital lobes expanding in the opposite area from the hydrogen atoms beyond the oxygen atom are observed by MO calculations [27]. The three point-model for water has been widely accepted after the successes achieved by *Matsuoka, Clementi*, and *Yoshimine* [28] with various modifications for the electronic charge distribution and bond length in the water molecule.

The tilt of water molecules in the hydration shell is interpreted in terms of hydrogen bonding of the water molecule with water molecules on the second hydration shell. A non-zero tilt angle $(\theta > 0°)$ allows to form three hydrogen bonds, whereas zero angle ($\theta = 0°$; the dipole of a water molecule directs to the central ion) means only two hydrogen bonds, and thus the former can form a more stable hydration sphere than the latter. MD simulations for anionic hydration show that the dipole of water molecules is almost exactly directed towards the central anion $(\Psi = 0\text{–}10°)$. This results agrees well with the experimentally obtained tilt angle for Cl^- $(\Psi = 0\text{–}6°)$ (see Table 2).

Dynamic Properties of Water Molecules in Hydration Shells of Ions

In contrast to static properties, *i.e.* structures, of hydrated ions studied by XD, ND, EXAFS, and NMR which usually gave energetic information of ions in water, dynamic properties, such as the residence time and rotational behavior of water molecules in the hydration shells of ions, can be found from kinetic and dynamic studies of electrolyte solutions. NMR, QENS, and MD studies may provide such dynamic information of hydrated ions. The residence times of water molecules in the first hydration shell of various ions are summarized in Table 3.

In Table 3, τ_{H_2O} denotes the averaged residence time of a water molecule in the bulk. τ_O and τ_H represent the residence time of oxygen and hydrogen atoms, respectively, of a water molecule in the first hydration shell of an ion. τ_H is usually smaller than τ_O due to the proton transfer reaction between the first hydration shell and a nearest neighbor water molecule:



$$M\cdots\underset{\mathrm{H}}{\underset{|}{\mathrm{O}}}-\mathrm{H}\cdots\underset{\mathrm{H}}{\underset{|}{\mathrm{O}}}-\mathrm{H} \Leftrightarrow M-\underset{\mathrm{H}}{\underset{|}{\mathrm{O}}}{}^{-}\cdots\mathrm{H}-\underset{\mathrm{H}}{\underset{|}{\mathrm{O}}}{}^{+}-\mathrm{H}$$

τ_{H_2O} is evaluated to be $(4.6 \pm 0.3) \times 10^{-12}$ s. The value of τ_O depends remarkably on the kind of ion. The value is very small for inert ions such as Cr^{3+} and Al^{3+}, but

Table 3. Residential time of water molecule in the bulk and of oxygen and hydrogen atoms of hydrated water molecules in the first hydration shell of ions (τ_{H_2O}, τ_O, and τ_H)

Ion	τ_{H_2O}/s	τ_O/s	τ_H/s	Method[a]	Ref.
Li^+	4.8×10^{-12}			MD	[1]
		3.3×10^{-11}		MD	[1]
			$\sim 3 \times 10^{-11}$	NMR	[2]
Na^+	3.8×10^{-12}	9.9×10^{-12}		MD	[1]
K^+	4.8×10^{-12}	4.0×10^{-12}		MD	[1]
		$< 10 \times 10^{-10}$		QENS	[3]
Cs^+		$< 10 \times 10^{-10}$		QENS	[3]
Be^{2+}		$\geqq 3 \times 10^{-4}$		NMR	[4]
Mg^{2+}		2×10^{-6}		NMR	[5]
			$\geqq 5 \times 10^{-5}$	QENS	[3]
Ca^{2+}		$< 10^{-10}$		NMR	[5]
			$\leqq 10 \times 10^{-10}$	QENS	[3]
Mn^{2+}		3.2×10^{-8}		NMR	[6]
Fe^{2+}		3.13×10^{-7}		NMR	[6]
Co^{2+}		8.8×10^{-7}		NMR	[6]
Ni^{2+}		3.7×10^{-5}		NMR	[6]
			$\geqq 5 \times 10^{-9}$	QENS	[3]
		1×10^{-4}		NMR	[6]
Cu^{2+}		5×10^{-9}		NMR	[6]
			$\leqq 10^{-10}$	QENS	[3]
Zn^{2+}			$> 10^{-10}$	QENS	[7]
Ti^{3+}		1.0×10^{-5}		NMR	[8]
V^{3+}		6×10^{-4}		NMR	[9]
		$1.8–2.2 \times 10^{5}$		NMR	[10]
Cr^{3+}			2×10^{-6}	NMR	[2]
			$\geqq 5 \times 10^{-9}$	QENS	[11]
Fe^{3+}		6×10^{-3}		NMR	[12, 13]
			$\geqq 5 \times 10^{-9}$	QENS	[14]
Co^{3+}		10^{5}		NMR	[15]
Al^{3+}		0.78		NMR	[16]
			$\geqq 5 \times 10^{-9}$	QENS	[14]
Ga^{3+}		5.5×10^{-5}		NMR	[8]
			$\geqq 5 \times 10^{-9}$	QENS	[14]
Nd^{3+}			$> 10^{-10}$	QENS	[3]
Tb^{3+}		$1.3–4.8 \times 10^{-8}$		NMR	[17]
Dy^{3+}		$3.1–7.1 \times 10^{-8}$		NMR	[17]
			$> 10^{-10}$	QENS	[14]
Ho^{3+}		$1.6 \times 10^{-8}–1.1 \times 10^{-7}$		NMR	[17]
Er^{3+}		$7.4 \times 10^{-9}–1.9 \times 10^{-7}$		NMR	[17]
Tm^{3+}		$1.5–3.0 \times 10^{-7}$		NMR	[17]
F^-	5.5×10^{-12}	20.3×10^{-12}		MD	[1]
			$\leqq 10^{-10}$	QENS	[3]
Cl^-	4.1×10^{-12}	4.5×10^{-12}		MD	[1]
			$\leqq 10 \times 10^{-10}$	QENS	[3]

[a] MD: molecular dynamics simulations, QENS: quasi-elastic neutron scattering

τ_O of alkali ions is close to that of bulk water. Generally speaking, among ions in the same group (in the same column of the periodic table), the larger the ionic radius, the smaller the τ_O value. The result coincides with considerations made by *Samoilov* [22]. Irregularity in the order of the magnitude of the τ_O values observed with the first transition metal ions have been explained by the ligand field theory applied to the stability of penta- or heptacoordinated reaction intermediates [29].

Studies on the dynamic behavior of hydrated water molecules have first been examined by relaxation methods such as temperature and pressure jumps as developed by *Eigen* and coworkers [25], but in recent years dynamic properties of hydrated water molecules have mostly been investigated by the NMR method. Exchange reactions of water molecules in the hydration shell of simple ions have been thoroughly investigated; the results are summarized in Table 4.

Activation enthalpies ($\Delta H^{\neq}$) and activation entropies ($\Delta S^{\neq}$) of water exchange reactions of hydrated ions can be obtained by measuring the temperature dependence of the rate constant of the reaction. Activation volumes ($\Delta V^{\neq}$) of the reaction can be determined by the pressure dependence of the rate constant.

$$(\mathrm{d}\ln k/\mathrm{d}T)_p = -\Delta H^{\neq}/RT + \Delta S^{\neq}/R \tag{1}$$

$$(\mathrm{d}\ln k/\mathrm{d}p)_T = -\Delta V^{\neq}/RT \tag{2}$$

$\Delta V^{\neq}$ is considered more reliable than $\Delta S^{\neq}$ with respect to value and even sign because the latter is obtained by an extrapolation of measured values to $1/T = 0$.

Mechanisms of exchange reactions of hydrated water molecules have been classified into three groups: Dissociative (D), Associative (A), and Interchange (I) mechanisms. Introduction of additional two mechanisms (Dissociative Interchange (I_d) and Associative Interchange (I_a)) between the two extremes allows to represent the reaction mechanisms more precisely.

Reaction kineticists often simply assign reactions with large negative values of $\Delta S^{\neq}$ or $\Delta V^{\neq}$ to the association mechanism, whereas reactions having large positive values of $\Delta S^{\neq}$ or $\Delta V^{\neq}$ should be dissociative. In the former reaction, a water molecule associatively attached to the hydration shell from the bulk should reduce the volume by *ca.* $-18\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ at the formation of an intermediate hydrated ion with an increased hydration number. On the other hand, release of a water molecule from the hydration shell due to the dissociation of a water molecule from the hydrated ion should result in an increase of volume by about $+18\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$. In the interchange reaction, $\Delta S^{\neq}$ and $\Delta V^{\neq}$ should be very small and close to zero. However, the classification of reaction mechanisms from the activation parameters has no sound theoretical basis, and the conclusions are usually derived from the picture shown in Fig. 1.

The picture shows that in the dissociative mechanism (D-Mechanism) the total volume of the hydrated ion with a loss of one water molecule and one water molecule in the bulk should be larger than that of the original hydrated ion. The reverse might hold for the associative mechanism (A-Mechanism) provided the volume of the hydrated ion does not change during the change in the hydration number of the ion. It is a well-known fact that the length of an ion-ligand bond increases when the coordination number increases and decreases with the decrease in the coordination number for a given ion with a given ligand. Therefore, an ion

Table 4. Rate constants of water exchange reactions of hydrated cations and thermodynamic parameters of the reaction at 25°C

Ion	Hydration Number n	k/s^{-1}	$\Delta H^{\neq}/\mathrm{kJ \cdot mol^{-1}}$	$\Delta S^{\neq}/\mathrm{kJ \cdot mol^{-1}}$	$\Delta V^{\neq}/\mathrm{cm^3 \cdot mol^{-1}}$	Reaction mechanism[a]	Ref.
Be^{2+}	4	7.3×10^2	59.2	8.4	−13.6	A	[1]
V^{2+}	6	8.7×10^1	61.8	−0.4	−4.1	I_a	[2]
Mn^{2+}	6	2.1×10^7	32.9	5.7	−5.4	I_a	[3]
Fe^{2+}	6	4.39×10^6	41.4	21.2	3.8	I_a–I_d	[3]
Co^{2+}	6	3.18×10^6	46.9	37.2	6.1	I_a–I_d	[3]
Ni^{2+}	6	3.37×10^4	52.3	17.2	7.1	I_d	[4]
Cu^{2+}	4	1×10^4	192	−16.8			[5]
	2	2×10^8	87.8				
Zn^{2+}	6	3×10^7					[6]
Ru^{2+}	6	1.8×10^{-2}	87.8	16.1	−0.4	I	[1]
Pd^{2+}	4	5.6×10^2	49.5	−26	−22	I_a or A	[6]
Pt^{2+}	4	3.9×10^{-4}	89.7	−9	−4.6	I_a or A	[1, 7]
Al^{3+}	6	1.29	84.7	41.6	5.7	I_d	[8]
Ga^{3+}	6	4×10^2	67.1	30.1	5.0	I_d	[9]
Ti^{3+}	6	1.8×10^5	43.4	1.2	−12.1	I_a or A	[9]
V^{3+}	6	5×10^2	49.4	−27.8	−8.9	I_a	[10]
VO^{2+}	5	7.41×10^2	55.6	−6.3			[11, 12]
Cr^{3+}	6	2.4×10^{-6}	108.6	11.6	−9.6	I_a	[13]
Fe^{3+}	6	6.8×10^4	40.3	80	−5.4	I_a	[14]
Ru^{3+}	6	3.5×10^{-6}	89.8	−48.3	−8.3	I_a	[1]
Rh^{3+}	6	2.2×10^{-9}	131.2	29.3	−4.2	I_a	[1]
Gd^{3+}	8	11.9×10^8	12.0	−30.9		I_a	[15]
Tb^{3+}	8	5.58×10^8	12.1	−36.9	−5.7	I_a	[16]
Dy^{3+}	8	4.34×10^8	16.6	−24.0	−6.0	I_a	[16]
Ho^{3+}	8	2.14×10^8	16.4	−30.5	−6.6	I_a	[16]
Er^{3+}	8	1.33×10^8	18.4	−27.8	−6.9	I_a	[16]
Tm^{3+}	8	0.47×10^8	22.7	−16.6	−6.0	I_a	[16]
Yb^{3+}	8	0.47×10^8	23.3	−21.0		I_a	[15]

[a] A: association mechanism, I: interchange mechanism, I_a: associative interchange mechanism, I_d: dissociative interchange mechanism, I_a–I_d: not distinguishable between I_a and I_d mechanisms

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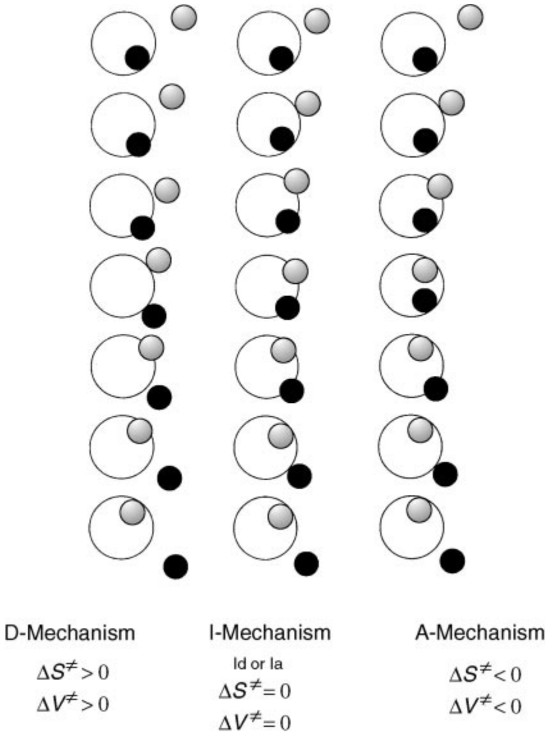


Fig. 1. Reaction mechanisms suggested from the values of activation entropies and activation volumes

with an increased hydration number formed at the intermediate step of the association mechanism in the water exchange reaction should have a larger volume than that of the original hydrated ion, and the reverse is true for an intermediate hydrated ion formed at the intermediate stage of the dissociation mechanism. The change in the volume of hydrated ions at the intermediate step of the reaction may hardly be estimated, but we cannot ignore the shrink in the volume of ions at the dissociation mechanism and inflation of the volume of an ion at the association mechanism. The volume change at the formation of an intermediate may be rather safely neglected for small ions such as hydrated multivalent transition metals, but for large ions coordinated with bulky ligands discussion of the reaction mechanisms from the data of $\Delta V^{\neq}$ should be very careful, and sometimes an erroneous conclusion may be derived.

A similar discussion can be made for the value of $\Delta S^{\neq}$. Vibrational and rotational motions of hydrated water molecules may not remain unchanged during water exchange reactions. Elongation of the metal-ligand bonds may enhance molecular motions in the hydration shell, which should increase in the entropy of the associatively formed intermediate. The loss in entropy of water molecules at the introduction to the hydration shell from the bulk should be more or less compensated by the increase in entropy due to the bond elongation. The reverse consideration can be made for the dissociation mechanism. Therefore, one should be very careful when discussing the reaction mechanism on the basis of thermodynamic quantities.

In fact, theoretical studies on water exchange reaction mechanisms of divalent and trivalent transition metal ions of the first transition period on the basis of SCF computational analysis [30, 31] lead to the conclusion that the reaction mechanism should be dissociative for Mn^{2+} and V^{2+} and trivalent ions such as Ti^{3+}, V^{3+}, Cr^{3+}, Fe^{3+}, and Ga^{3+}, which is not compatible with the associative interchange mechanism proposed for these ions on the basis of their negative activation volumes $\Delta V^{\neq}$.

Ionic Hydration under Extreme Conditions

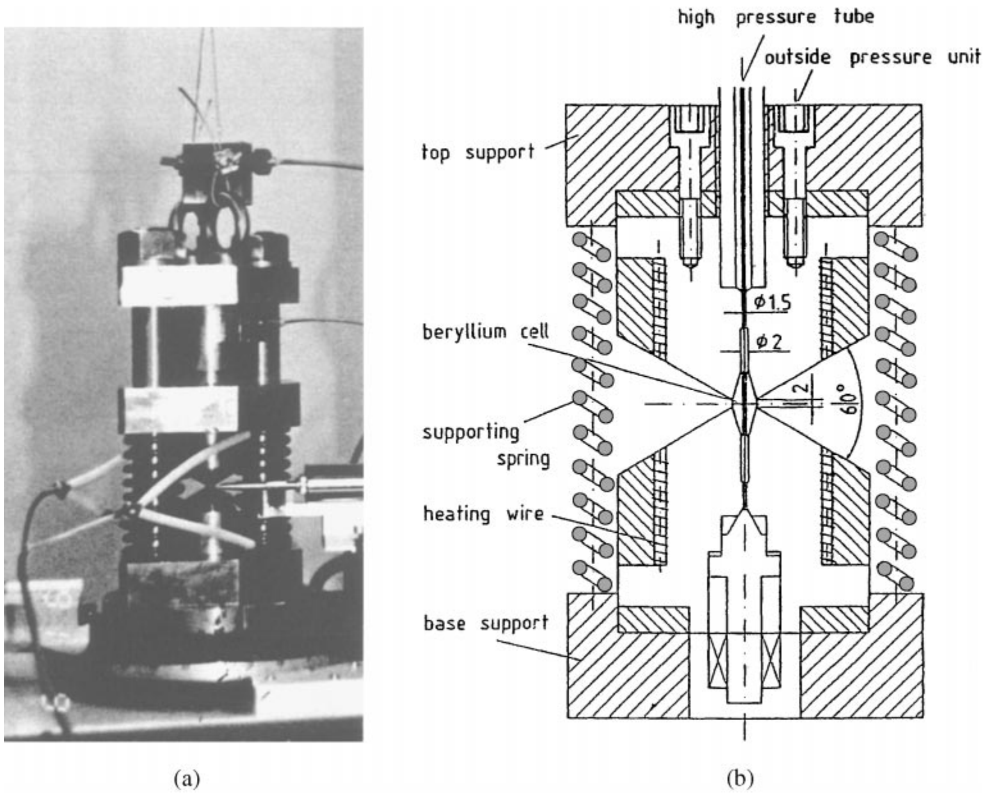
Numerous studies have been carried out on the structure of water since 1930 after XD studies by *Mayer* [14], *Stewart* [15], and *Amaldi* [16] and the theoretical work by *Bernal* and *Fowler* [17]. The water structure at supercooled temperatures and in the glassy state has also been investigated from the viewpoints of chemistry, physics, geology, biology, and engineering [32, 33]. Water can remain liquid below 0°C at 1 atmosphere pressure and is then believed to have a similar structure like water under normal conditions. Glassy water, which has deformed hydrogen bonds, is formed by quick quenching of liquid water.

Water under supercritical conditions ($t_c = 374.2°C$, $p_c = 22.1\,\mathrm{MPa}$, $\rho_c = 0.3228\,\mathrm{g \cdot cm^{-3}}$) has attracted much interest not only in the fields of chemistry and physics, but also geology in connection of underground waters, biology from the knowledge of evolution of life, and engineering for decomposing organohalogeno compounds and synthesis of organic and inorganic compounds.

The structure of water at high temperatures and high pressures, especially under supercritical conditions, has been extensively investigated by many authors employing various methods, and the conclusions derived from these studies are rather divergent. However, in recent years, the solution X-ray diffraction technique with a special cell arrangement has effectively been applied to structural studies at high temperatures and high pressures (HTHP), and the conclusions on the structure of water in the supercritical region seem to indicate that supercritical water consists of small clusters containing hydrogen-bonds and monodispersed gas-like water molecules. An HTHP cell used for XD studies of water is shown in Fig. 2. Recent studies on the structure of supercritical water have been summarized in some articles [34, 35].

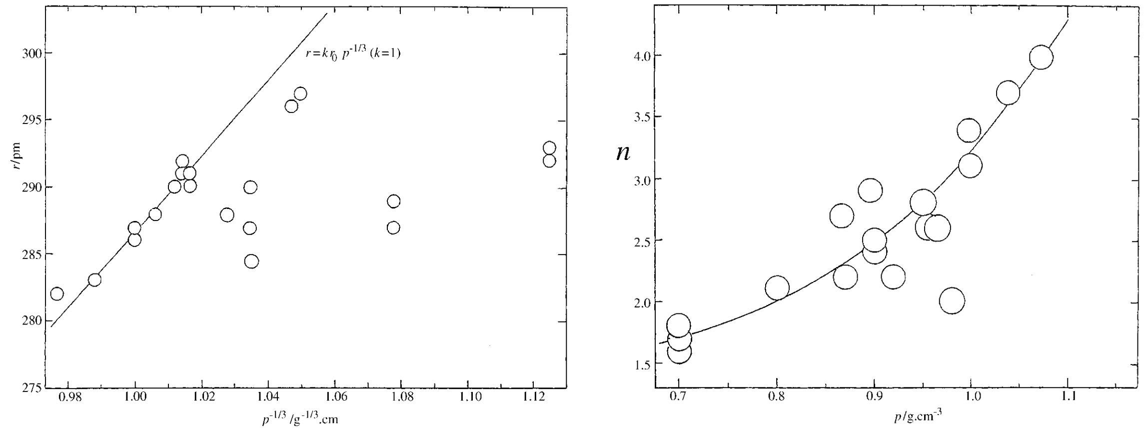
According to XD studies [34–36], the water-water distance slightly increased with decreasing density (expansion of water due to decreasing density) from 282 pm at $1.09\,\mathrm{g \cdot cm^{-3}}$ to 291 pm at $0.75\,\mathrm{g \cdot cm^{-3}}$; then the water-water distance is kept practically unchanged with further decreasing water density down to $\rho = 0.71\,\mathrm{g \cdot cm^{-3}}$. On the other hand, the number of nearest water molecules (the coordination number n) monotonously decreases with decreasing water density. The coordination number n of a water molecule is 4.4 at ambient temperature and pressure with $\rho = 1\,\mathrm{g \cdot cm^{-3}}$, and n decreases to 1.7 at $\rho = 0.71\,\mathrm{g \cdot cm^{-3}}$ (Fig. 3). From these results it can be concluded that water forms small clusters, in which relatively few water molecules are bound to each other through hydrogen bonds; the size of the cluster may decrease with temperature, and some other water molecules may be almost monomerly dispersed to form a gas-like phase.

It has been stated that the solubility of electrolytes decreases in supercritical water compared with that in normal water, in contrast to the increased solubility of



(a) (b)

Fig. 2. A high temperature-high pressure cell for X-ray diffraction experiment of liquids; (a): photograph of the cell, (b): construction and dimensions of the cell



(a) (b)

Fig. 3. The nearest water-water distance r and the coordination number n at high temperatures and high pressures; (a): distance r plotted against $\rho^{-1/3}$; the straight line is drawn on the basis of the equation, $r = kr^0 \cdot \rho^{-1/3}$ where r^0 denotes the water-water distance in normal water at ambient conditions and $k = 1$; ρ represents the density of water; (b): number of water molecules at the nearest neighbor, n plotted against ρ

nonelectrolytes which hardly dissolve in water under ambient conditions. However, this expression is not clear, because the statement does not take into account the decreased density of water under supercritical conditions. It is obvious that hydration of electrolytes must be reduced in water of low density, and non-electrolytes, which are not well hydrated by water, can mix with gaseous water. Therefore, comparison between solubilities of electrolytes and non-electrolytes in supercritical water must be made at the same density of water. It is not easy to study the structure and properties of electrolyte solutions at supercritical temperatures and pressures by keeping the water density close to unity. The behaviour of hydrated ions in supercritical water has not been investigated so extensely, and a rather limited number of results have been reported. Some examples are given in the following sections.

The strontium(II) ion combines with 7.3 water molecules in aqueous 0.2 mol · dm^{-3} $Sr(NO_3)_2$ solution at room temperature, but it has only 3.5 water molecules at 385°C and 27 MPa [37]. However, it should be noted that the density of water at 385°C and 27 MPa is very low (about 0.4 g · cm^{-3}).

An EXAFS study [38] on a dilute aqueous solution of $NiBr_2$ showed that the coordination number of Ni^{2+} of 6.1 at normal conditions decreased to 2.6 at 425°C and 68.1 MPa, and a fairly large amount of Ni^{2+}–Br^- ion pairs with a Ni^{2+}–Br^- distance of 240 pm were formed. The length of the Ni^{2+}–O bonds of the hydrated nickel(II) ion in the supercritical water was found to be 209.5 pm, much longer than the Ni^{2+}–O bond length of 204 pm in a 0.1 mol · dm^{-3} solution at room temperature [10]. The density of water under these conditions is 0.65 g · cm^{-3}, and thus the concentration of water is only about 2/3 of that of normal water. A very similar result was obtained for a 0.2 mole · dm^{-3} solution of $NiBr_2$, the result indicating that the concentration dependence of the coordination number and the bond length is not significant. In the solution of $NiBr_2$ it was found that the hydration number of the nickel(II) ion decreased with increasing temperature and pressure, but the decrease in the hydration number may be more simply described in terms of the decrease in the density of water in the solution.

Ionic Solvation in Nonaqueous Solvents

Since most electrolytes are less soluble in nonaqueous solvents than in water, solvation phenomena of ions in nonaqueous solution have been much less investigated compared to those in aqueous solution. However, nonaqueous solutions of electrolytes have been interesting for physical chemists in understanding ion-molecule interactions and recognizing their importance in various industries such as material production, electrolysis, and metal plating. Furthermore, ionic solvation in nonaqueous solvents has attracted the interest of electrochemists, physical chemists, and analytical chemists as the most fundamental phenomenon of nonaqueous solution chemistry. With the development of methods for its investigation, various studies on structure and dynamics of electrolytes in nonaqueous solvents have been attempted.

Many alcohols and some nonaqueous solvents such as N,N-dimethylformamide (*DMF*), dimethyl sulfoxide (*DMSO*), or acetonitrile (*AN*) have medium relative dielectric constants of $\varepsilon_r = 35$–46 between high (water) and low (benzene and *n*-hexane) dielectric solvents, and many electrolytes can be dissolved in these solvents. The donor and acceptor properties of these medium dielectric solvents are comparable with those of water (donor numbers $D_N = 20–30$, acceptor numbers $A_N = 20–40$; water: $D_N = 18.0$, $A_N = 54.8$); thus, donor-acceptor interactions between ions and solvent molecules can be compared with those with water molecules to make the electrolyte soluble. Thermodynamic studies on electrolyte solutions in nonaqueous solvents have thus been explored rather widely [4]. Thermodynamic data are, of course, very important to understand the solution behavior of electrolytes in solvents, but they do not give a clear picture about the solvation structure. On the contrary, NMR, XD, ND, and EXAFS can provide definitive information about the solvation structure of individual ions in solution. Thermodynamic and structural data are complementary to each other, and both are indispensable for understanding the solution chemistry of electrolytes in nonaqueous solvents. However, unfortunately, compared with thermodynamic data, structural data for nonaqueous solutions are rare.

Studies the on solvation structure of ions in nonaqueous solvents have been recently attempted by using molecular dynamics simulations, but few results have been reported so far and are less reliable because the potential functions employed in the calculations were not highly polished.

The copper(II) ion forms a distorted octahedral structure in aqueous solution [23], and the ion has a similar distorted octahedral structure in *DMF* with Cu–O_{eq} and Cu–O_{ax} distances of 201–203 and 284–287 pm, respectively [39]. It has been found by an EXAFS measurement that the nickel(II) ion forms an octahedral solvation structure in various nitriles such as acetonitrile, propionitrile, butyronitrile, isobutyronitrile, valeronitrile, and benzonitrile similar to water [40]. The length of the Ni–O bond in the nitriles is 205.0–206.9 pm, which is not significantly different from the Ni–O bond length found in water (204–205 pm [40–42]).

1,3-Propanediamine (trimethylenediamine) is a bidentate ligand with two nitrogen atoms in a molecule of strong donor property. The cobalt(II) ion in 1,3-propanediamine combines with three solvent molecules to form an octahedral hexacoordinated solavte [43]. The Co–N bond length is 217 pm, which is longer than that in water in which the Co–O bond amounts to 208 pm [41, 43]. The difference in the bond lengths may arise from the bidentate character of the formation of a five-membered ring of the solvent rather than from the different atomic sizes of nitrogen and oxygen atoms in 1,3-propanediamine and water, respectively. In *n*-propylamine, the cobalt(II) ion forms an equilibrium mixture of octahedral hexacoordinated and tetrahedral tetracoordinated solvates [43]. The Co–N bond length is the same as in 1,3-propanediamine for the octahedral species, but the length in the tetrahedral one is 201 pm.

In a bulky solvent such as 1, 1, 3, 3-tetramethylurea (*TMU*) ions often cannot form an octahedral structure due to steric hindrance between ligating solvent molecules. The cobalt(II) ion forms a tetracoordinated solvate in *TMU* [44].

The solvation structure of lanthanide ions (Ln^{3+}) in *DMF* and N,N-dimethylacetamide (*DMA*) has been compared using the EXAFS method; no significant difference was observed [45].

The silver(I) ion can form various coordination structures depending on the coordinating solvent and the ligand molecules. Hard and soft properties of ligand atoms also affect the coordination structure of solvates of the silver(I) ion. The silver(I) ion forms a tetracoordinated solvate in oxygen-donating solvents such as water [46–48] and *DMF* [49] and in nitrogen-donating ones such as ammonia [50], acetonitrile [49–51], and pyridine [50, 52]. The Ag–N bond length was determined to be 224–226 pm [49, 50] in *AN* and 232 pm [52] in pyridine, which is slightly shorter than the Ag–O bond length (237–240 pm [46–48]).

The solvation structure of the silver(I) ion in *DMSO* is not conclusive at the present stage of investigation. It has been found that Ag^+ forms a tetrahedral structure in *DMSO* with four Ag–O bonds in the first coordination solvation shell by means of EXAFS [53]. On the other hand, a Ag–N bond together with three Ag–O bonds has been observed in the same solvent by XD [54]. Recently, *Persson* [55] reported that he did not find the Ag–N bond, and that the $[Ag(DMSO)_4]^+$ ion shows only the four Ag–O bonds. The structural analysis of the Ag^+ solvate in *DMSO* is presently repeated. Structural data of solvated ions in typical nonaqueous solvents are summarized in Table 5.

Preferential Solvation of Ions in Mixed Solvents

Mixed solvents have widely been used in thermodynamic, dynamic, and kinetic studies on ionic interactions in solution with changing solvent properties of the reaction medium. Dielectric constants and viscosities of solvents are changed by varying solvent composition of the mixtures. Theories proposed for explaining the variation of the thermodynamic, dynamic, and kinetic data usually assumed a homogeneous continuum with specific bulk properties, and theories which can be successfully applied to a neat medium usually fail in mixed solvent systems. The *Born* equation is not valid in other solvents than water for the calculation of solvation energies of ions, and activity coefficients in nonaqueous and mixed solvents calculated by using the *Debye-Hückel* equation do not agree with those determined experimentally. Conductivities of an ion in isoviscous mixed solvents are usually not constant. The disagreement of theoretical values with experimental ones has been traced to the inadequacy of the simple continuum assumption. The different solvent composition in the solvation shell from that in the bulk may be another important factor for causing the discrepancies.

It can easily be expected that in a mixed solvent, in which one solvent has a larger solvation affinity to an ion than the other, the former solvent may be preferentially solvated with the ion than the latter. However, there is no proper method to determine the solvent composition in the neighbourhood of an ion. The XD method can be a suitable tool to determine the solvent composition of the first solvation shell of ions. The EXAFS method, if it could be applied to mixed solvent systems of ions in an accurate and reliable way, could be useful. *Raman* spectroscopy is another powerful tool for the investigation of preferential solvation of ions.

Acetonitrile (*AN*; *Gutmann*'s donor number: $D_N(AN) = 14.1$; *Gutmann-Mayer*'s acceptor number: $A_N(AN) = 19.3$) and N,N-dimethylformamide (*DMF*; $D_N(DMF) = 26.6$, $A_N(DMF) = 16.0$) are both aprotic solvents of medium dielectric constants. In *AN-DMF* mixtures, the silver(I) ion forms $[Ag(AN)_4]^+$, $[Ag(AN)(DMF)_3]^+$, $[Ag(AN)_2(DMF)_2]^+$, $[Ag(AN)_3(DMF)]^+$, and $[Ag(DMF)_4]^+$ species depending on the solvent composition [49]. The Ag–O (*DMF*) bond length

Table 5. Selected values of ion-ligand atom distances (r_{M-X}) and number of solvent molecules (n) coordinated the ion in various solvents

Ion	*DMSO*		*DMF*		*DMA*		*AN*		*DMTF*		*DMPU*		P_y		*PDA*	
	r/pm	n	r/pm	n	r/pm	n	r/pm	n	r/pm	n	r/pm	n	r/pm	n	r/pm	n
Ca^{2+}	232	6	229	6												
Sr^{2+}	254	6									255	6				
Ba^{2+}	276	6									275	6				
Cu^{+}	209	4					199	4	233[m]	4						
Ag^{+}	224[a] 257[b]	4	233	4			226	4	255[m]	4	241	4				
Au^{+}							219	4	228[m]	4			216	4		
Mn^{2+}							220	6			210	5				
Fe^{2+}	210	6					214	6			202	4				
Co^{2+}	209.5	6	213	6			211.6	6			200	5			217	6
Ni^{2+}	206.3	6					206.7	6			200	5				
Cu^{2+}	198[d] –	6[c]	201[d] 284	6[c]			199[d] –	6[c]			192	4[i]				
Zn^{2+}	212	6					208	6	236[m]	4	195	4				
Cd^{2+}	229	6	230	6					270[m]	6	229	6				
Hg^{2+}	239	6[e]							257.2[m]	4						
Hg_2^{2+}	222[f]	4					221[k]	2[l]			222	4				
Sn^{2+}									267 –	4[g]						
Pb^{2+}									289	6						
Pd^{2+}	204[h] 223	4[i]														
Pt^{2+}	207[h] 221.5	4[i]					200	4[i]	230	4[i]						
Sc^{3+}	209	6														
Fe^{3+}	202	6														
Y^{3+}	236	8[j]									224	6				

Bi^{3+}	241	8^j					279	6	232	8
La^{3+}	250	8^j	248.6	7.3	247.5	6.5	244	~7		
Ce^{3+}			247.4	8.1	245.2	6.6				
Pr^{3+}			244.7	7.4	242.0	6.9				
Nd^{3+}			243.8	7.4	240.2	6.1				
Sm^{3+}			241.6	8.9	236.7	8.4				
Eu^{3+}			238.5	7.7	234.7	6.7				
Gd^{3+}			238.5	7.5	233.3	7.2				
Tb^{3+}			236.9	7.5	231.9	7.3				
Dy^{3+}			236.0	7.7	230.5	7.0				
Ho^{3+}			234.6	7.8	229.3	6.9				
Er^{3+}			233.6	7.2	227.3	7.6				
Tm^{3+}			232.5	7.5	226.7	6.8				
Yb^{3+}			230.9	7.5	223.8	6.3				
Lu^{3+}			229.8	7.9	222.1	6.0				
Ga^{3+}	196	6					224	4	192	5
In^{3+}	214	6					261	6	214	6
Bi^{3+}	241	8^j					279	6	233	6

DMSO: dimethyl sulfoxide; *DMF*: N,N-dimethylformamide; *DMA*: N,N-dimethylacetamide; *AN*: acetonitrile; *DMTF*: N,N-dimethylthioformamide; *DMPU*: 1,3-dimethylpropylene urea; *Py*: pyridine; *TMU*: tetramethylurea; *PDA*: 1,3-propanediamine; [a]three *M*–O bonds; [b]one *M*–S bond; [c]*Jahn-Teller* distorted octahedron; [d]four equatorial Cu–O bonds; [e]second-order *Jahn-Teller* distorted octahedron; [f]Hg–Hg bond length: 250 pm; [g]two bonds are longer than the other two; [h]two *M*–O bonds and two *M*–S bonds; [i]square-planar. [j]square antiprism; [k]Hg–Hg bond length: 254 pm; [l]linear; [m]*M*–S bond; [n]square pyramid; [o]bidentate ligand

Table 6. Preferential solvation of ions in binary **A–B** mixtures

Ion	Mole fraction of solvent **A** in the bulk	Main species in solution	Average metal-ligating atom distance *r*/pm	Mole fraction of solvent **A** in the first solvation shell
Ag^+	*AN-DMF* Mixture [1] ($\mathbf{A} = AN, \mathbf{B} = DMF$)			
	0.00	$[Ag(DMF)_4]^+$	Ag–O: 233	0.00
	0.15	$[Ag(AN)(DMF)_3]^+$	Ag–O: 235 Ag–N: 226	0.2(5)
	0.25	$[Ag(AN)_2(DMF)_2]^+$	Ag–O: 237 Ag–N: 224	0.5(0)
	0.33	$[Ag(AN)_2(DMF)_2]^+$	Ag–O: 237 Ag–N: 224	0.5(0)
	0.50	$[Ag(AN)_2(DMF)_2]^+ (\sim 50\%)$ $[Ag(AN)_3(DMF)]^+ (\sim 50\%)$	Ag–O: 237 Ag–N: 224 Ag–O: 241 Ag–N: 224	0.6(3)
	0.67	$[Ag(AN)_3(DMF)]^+$	Ag–O: 241 Ag–N: 224	0.7(5)
	1.00	$[Ag(AN)_4]^+$	Ag–N: 226	1.00
Ca^{2+}	*DMSO-DMF* Mixture [2] ($\mathbf{A} = DMSO, \mathbf{B} = DMF$)			
	0.00	$[Ca(DMF)_6]^{2+}$	Ca–O: 229	0.00
	0.25[a]	$[Ca(DMF)_4(DMSO)_2]^{2+}$ and/or $[Ca(DMF)_3(DMSO)_3]^{2+}$	Ca–O: 228–229	0.3(3)–0.5(0)
	0.50	$[Ca(DMF)_2(DMSO)_4]^{2+}$	Ca–O: 230	0.6(7)
	0.75	$[Ca(DMF)(DMSO)_5]^{2+}$	Ca–O: 232	0.8(3)
	1.00	$[Ca(DMSO)_6]^{2+}$	Ca–O: 232	1.00

[a] Not distinguishable between the two species, probably approximately 1:1 mixture to be formed

[1] Ozutsumi K, Kitakaze A, Iinomi M, Ohtaki H (1997) J Mol Liquids **73/74**: 385; [2] Ozutsumi K, Ikuno N, Suzuki T, Ohtaki H (1999) 49th National Conference on Coordination Chemistry, September, Sapporo, Japan

was determined to be 233–241 pm, whereas the Ag–N (*AN*) bond was 224–226 pm, and the Ag–O bond is gradually elongated by the stepwise addition of acetonitrile molecules to the solvation shell. The solvent composition of the first solvation shell of the main species formed in various *AN-DMF* mixtures, together with the lengths of individual Ag–O and Ag–N bonds, are summarized in Table 6. The accuracies of the results are not too high, but the variation of the solvent composition of the solvation shell with the composition in the bulk can be recognized.

It shall now be attempted to introduce a quantitative measure of preferential solvation of ions. When the solvent composition of an **A**-**B** mixture in the bulk is defined to be $[\mathbf{A}]_B$ and $[\mathbf{B}]_B$, where $[\ ]_B$ denotes the concentration of a solvent in the bulk (*e.g.* mole fraction), and the concentrations of solvents **A** and **B** in the first

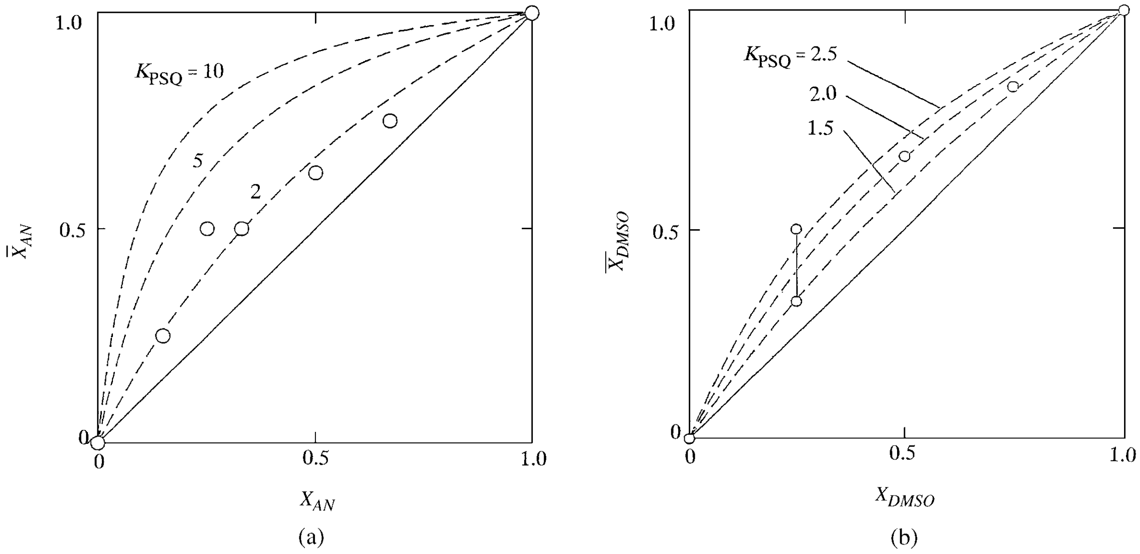


Fig. 4. Plots of mole fraction of a solvent **A** in the solvation shell, $\bar{x}_{\mathbf{A}}$, against mole fraction of solvent **A** in the bulk $x_{\mathbf{A}}$; (a): Ag(I) in *AN-DMF* mixtures; (b): Ca^{2+} in *DMSO-DMF*

solvation shell are denoted by $[\mathbf{A}]_{SS}$ and $[\mathbf{B}]_{SS}$, respectively, the preferential solvation quotient K_{PSQ} can be defined as follows:

$$K_{PSQ} = \frac{[\mathbf{A}]_{SS}/[\mathbf{B}]_{SS}}{[\mathbf{A}]_B/[\mathbf{B}]_B} = \frac{\bar{x}_{\mathbf{A}}/(1-\bar{x}_{\mathbf{A}})}{x_{\mathbf{A}}/(1-x_{\mathbf{A}})} \tag{3}$$

$\bar{x}_{\mathbf{A}}$ and $x_{\mathbf{A}}$ denote the mole fraction of solvent **A** in the first solvation shell and in the bulk, respectively. When K_{PSQ} is larger than unity, the ion is preferentially solvated with solvent **A**.

A plot of $\bar{x}_{AN}$ in the first solvation shell of the Ag^+ ion against x_{AN} in the bulk solvent is given in Fig. 4a. All experimental points fall on the line drawn of K_{PSQ} being about 2. If it is assume that the preferential solvation occurs due to the difference in the *Gibbs* energies of solvation of the two solvents towards the Ag^+ ion, the preferential solvation quotient can be given as the difference in the *Gibbs* free energies of solvation of *AN* and *DMF*, and the difference, $\Delta\Delta G^0_{\text{solv}}$, can be evaluated from the *Gibbs* free energies of transfer of the Ag^+ ion from water to *AN* and from water to *DMF*. Thus,

$$-RT\ln K_{PSQ} = \Delta\Delta G^0_{\text{solv}} = \Delta G^{\text{tr}}_{\text{Ag}}(H_2O \rightarrow AN) - \Delta G^{\text{tr}}_{\text{Ag}}(H_2O \rightarrow DMF) \tag{4}$$

Insertion of the reported values of $\Delta G^{\text{tr}}_{\text{Ag}}(H_2O \rightarrow AN)$ and $\Delta G^{\text{tr}}_{\text{Ag}}(H_2O \rightarrow DMF)$ (-23.2 and $-20.8\,\text{kJ}\cdot\text{mol}^{-1}$, respectively [4]) into Eq. (4) leads to $\Delta\Delta G^0_{\text{solv}} = -2.4\,\text{kJ}\cdot\text{mol}^{-1}$. The value of $-RT\ln K_{PSQ}$ at $K_{PSQ} = 2$ is $-1.7\,\text{kJ}\cdot\text{mol}^{-1}$, which is fairly close to the value of $\Delta\Delta G^0_{\text{solv}}$.

The calcium ion is a typical divalent cation. The solvation number of Ca^{2+} has been reported to be six or eight depending on solvent, temperature, and pressure. In *DMSO-DMF* mixtures the Ca^{2+} ion is preferentially solvated with *DMSO* over *DMF* (see Table 6 and Fig. 4b). The K_{PSQ} value estimated from the plot is about 2. Therefore, $-RT\ln K_{PSQ} = \Delta\Delta G^0_{\text{solv}}$ can be evaluated to be $-1.7\,\text{kJ}\cdot\text{mol}^{-1}$. The

Gibbs free energy of transfer of Ca^{2+} from *DMF* to *DMSO* has not been reported in the literature, but it may be roughly estimated from the values of alkali metal ions to be about -2–$-3\,\mathrm{kJ\cdot mol^{-1}}$ (-5.0 [Li^+], -3.8 [Na^+], -2.7 [K^+], -0.7 [Rb^+], and $-2.2\,\mathrm{kJ\cdot mol^{-1}}$ [Cs^+]), which is again close to the value evaluated from the plot of Fig. 4b ($-1.7\,\mathrm{kJ\cdot mol^{-1}}$). Therefore, it can be concluded that preferential solvation occurs due primarily to the difference in the *Gibbs* energies of solvation of the two solvents under examination [56].

Solvent-solvent interaction is another important factor controlling preferential solvation of ions. 1, 1, 3, 3-Tetramethylurea ($D_N(TMU) = 31$) is a much stronger donor solvent than water ($D_N(H_2O) = 18$), and thus *TMU* is expected to be preferentially solvated with cations over water. However, in H_2O-*TMU* mixtures with a larger proportion of water, the Co(II) ion preferentially solvated with water. The results can be explained in terms of strong *TMU*-H_2O ($A_N(H_2O) = 54.8$) intermolecular interactions in the bulk, which result in the disappearance of free *TMU*. In mixtures containing *TMU* as a major portion, Co(II) is preferentially solvated with *TMU* [57]. Specrtophotometric evidence shows that Co(II) forms a tetrasolvated $[Co(TMU)_4]^{2+}$ complex in neat *TMU* [57].

Yokoyama et al. [58] have determined the solvent composition in the solvation shell of Co^{2+} in various amide-water mixtures by XD, the plots of $\bar{x}_{\mathrm{amide}}$ against x_{amide} being shown in Fig. 5. The *Gibbs* free energy of solvation or *Gutmann*'s donor number of these amides cannot be significantly different, but they have different abilities for hydrogen-bonding with water molecules due to different numbers of

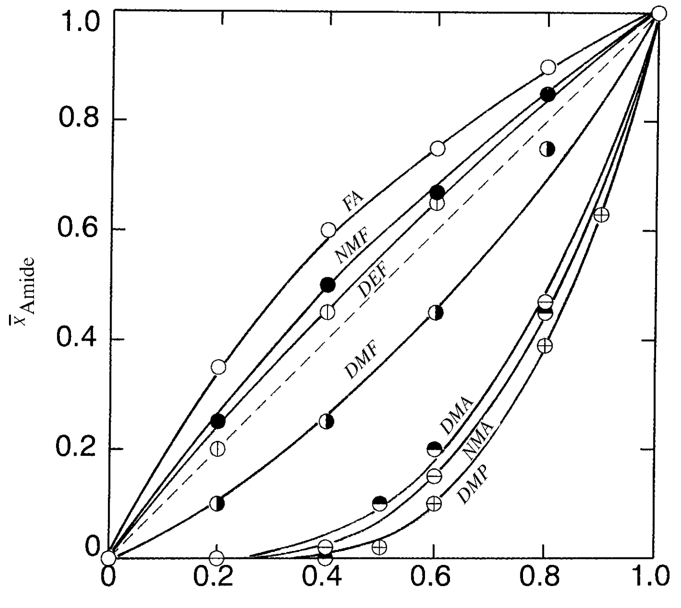


Fig. 5. Plots of mole fraction of an amide in the solvation shell, $\bar{x}_{\mathrm{Amide}}$, of Co(II) against mole fraction of the amide in the bulk x_{Amide}; ○: formamide (*FA*), ●: N-methylformamide (*NMF*), ⦶: N,N-diethylformamide (*DEF*), ◑: N,N-dimethylformamide (*DMF*), ◓: N,N-dimethylacetamide (*DMA*), ⊖: N-methylacetamide (*NMA*), ⊕: N,N-dimethylpropionamide (*DMP*); quoted from Ref. [57]

free amino groups in their molecules. Moreover, they have different substituents which result in different volumes of bulkiness of the molecules; this may cause a steric hindrance in the rather crowded solvation sphere of the ion. They explained their results primarily in terms of different solvation abilities of the amides, which may be more or less proportional to *Gutmann*'s D_N. The preferential solvation of formamide $(FA, D_N = 24)$ over water $(D_N = 18)$ can be evidence thereof. When amino protons are substituted with alkyl groups, the amino group in the molecule attracts a lower number of water molecules in the bulk, so that the concentration of free water molecules increases. Thus, Co^{2+} can be solvated with more water than amide molecules. This explanation is similar to that given for the behaviour of the cobalt(II) ion in *TMU*-H_2O mixtures [57]. The different volumes of solvent molecules with bulky substituents may be an additional reason for causing different degrees of preferential solvation of the amides. The reason why N,N-diethylformamide (*DEF*) is advantageous in preferential solvation over water compared with N,N-dimethylformamide (*DMF*) (see Fig. 5) is not clear, but hydrophobicity of the longer alkyl chains attached to the nitrogen atom in the former may play a significant role.

Raman spectroscopy can be another useful technique for the study of preferential solvation of ions. *Umebayashi et al.* [59] have applied the method to the determination of the total solvation number of various ions together with the composition of the solvent molecules in the first solvation shell. They determined the total number of solvated molecules in the first coordination sphere, as well as the numbers of individual solvent molecules of Mn(II), Ni(II), Cu(II), and Zn(II) in *DMF-DMA* and *DMF-TMU* mixtures. In Fig. 6 their results for Mn(II) in *DMF-DMA* and *DMF-TMU* (Figs. 6a and 6b, respectively) and for Ni(II) in *DMF-DMA* mixtures (Fig. 6c) are quoted [59].

It should be noted in that Mn(II) shows no preferential solvation in *DMF-DMA* mixtures in spite of the larger donor number of *DMA* $(D_N = 28.7)$ compared to *DMF* $(D_N = 26.6)$ (Fig. 6a). The result suggests that the energy lost due to the steric hindrance of bulky *DMA* in the first solvation shell may approximately be

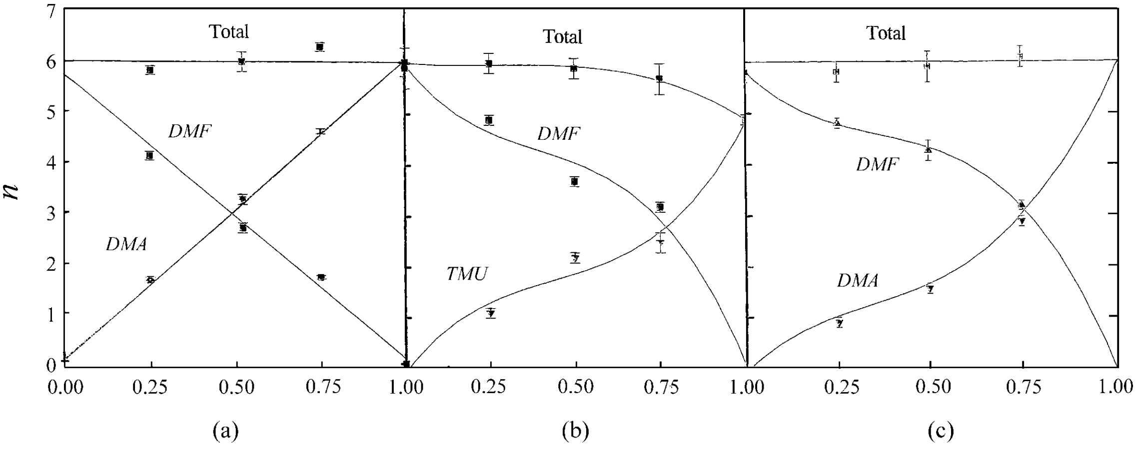


Fig. 6. Solvation of Mn(II) and Ni(II) in binary mixtures; (a): Mn(II) in *DMF-DMA*, (b): Mn(II) in *DMF-TMU*, (c): Ni(II) in *DMF-DMA*; quoted from Ref. [58]

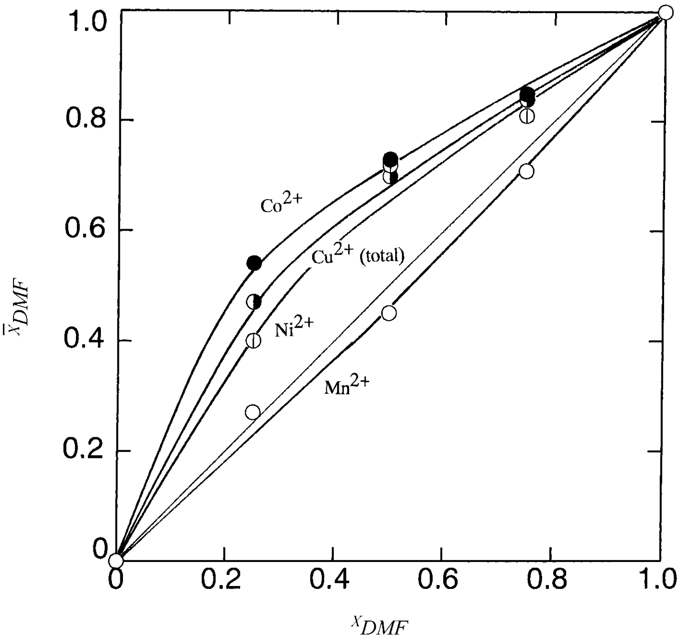
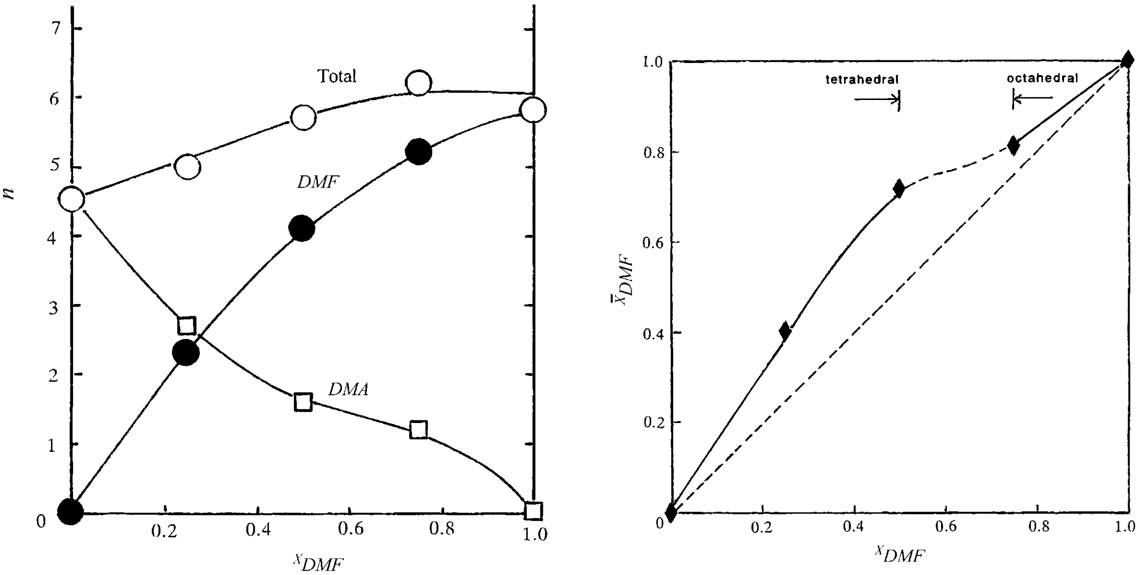


Fig. 7. Plots of mole fraction of *DMF* in the solvation shell, $\bar{x}_{DMF}$, of divalent transition ions against mole fraction of *DMF* in the bulk, x_{DMF}; Co^{2+} (●), Cu^{2+} (total) (◑), Ni^{2+} (⦶), and Mn^{2+} (○); quoted from Ref. [61]

compensated by an energy proportional to the difference in the donor properties of the two solvents $(2.1\,\text{kcal}\cdot\text{mol}^{-1} = 5.0\,\text{kJ}\cdot\text{mol}^{-1})$. The steric effect caused by the bulky methyl group in *DMA* may hinder the rotation of the *DMA* molecule in the solvation sphere along the -C–N- axis, which may result in a decrease in the entropy of solvation which is more pronounced for *DMA* than for *DMF*. Therefore, $\Delta\Delta G^0_{\text{solv}}$ of the Mn(II) ion should be much less than the expected value from the difference in D_N of *DMA* and *DMF*. The bulkier *TMU* $(D_\text{N} = 31)$ is less preferentially solvated to the Mn(II) ion than *DMF* in spite of a larger donor property in the former (Fig. 6b). The bulkiness of the substitutents in *TMU* causes a decrease in the total solvation number of Mn(II). In the case of Ni(II) (see Fig. 6c), the total solvation number of Ni(II) remains unchanged over the whole composition range, and *DMF* is preferentially solvated to the Ni(II) ion than *DMA*. Again, *DMA* with its larger donor number is less preferred by the Ni(II) ion due to its bulky volume.

Plots of $\bar{x}_{DMF}$ *vs.* x_{DMF} in *DMF-DMA* mixtures recalculated from the data reported by *Umebayashi et al.* [59] for Co^{2+}, Cu^{2+}, Ni^{2+}, and Mn^{2+} are shown in Fig. 7. All these ions have an octahedral structure, although the structure of the Cu^{2+} ion is distorted by the *Jahn-Teller* effect, an effect which will be discussed in more detail later. The order of preferential solvation of *DMF* over *DMA* is $Co^{2+} > Ni^{2+} \gg Mn^{2+}$. *Umebayashi* and coworkers [59] have explained the smallest preferential solvation of Mn^{2+} (ionic radius: 81 pm) in terms of the large size of the ion. However, Co^{2+} (79 pm) has a larger ionic size than Ni^{2+} (70 pm).

The behavior of the zinc(II) ion is unique in *DMF-DMA* mixtures. It has been observed that the coordination number of the Zn(II) ion decreases from six in neat *DMF* to four in neat *DMA* (Fig. 8a), which shows that the Zn(II) ion prefers *DMF*



(a) (b)

Fig. 8. Solvent composition in the solvation shell of Zn(II) ion in *DMF-DMA* mixtures; (a): total number of solvent molecules in the first solvation shell and the numbers of individual solvents; (b): $\bar{x}_{DMF}$ *vs.* x_{DMF}; quoted from Ref. [61]

over *DMA* in spite of a larger donicity of *DMA* [59]. A plot of $\bar{x}_{DMF}$ *vs.* x_{DMF} (Fig. 8b) gives a curve with an inflexion point around $x_{DMF} = 0.5$–0.7, probably due to the change in the coordination structure from octahedral to tetrahedral.

The enthalpy of transfer, $\Delta H^{\mathrm{tr}}_{\mathrm{Mn}}(DMF \rightarrow DMA)$, of Mn(II) from *DMF* to *DMA* at 25°C [60] is negative ($-6.9\,\mathrm{kJ \cdot mol^{-1}}$), but the values of other divalent ions are positive (7.9 for Co(II), 17.4 for Ni(II), and $21.8\,\mathrm{kJ \cdot mol^{-1}}$ for Zn(II)). The results show that divalent metal ions, except for Mn(II), are stabilized in *DMF* better than *DMA*, which is contrary to a result expected from the solvation abilities of *DMF* and *DMA*.

Solvation of Cu(II) changes in a rather complicated way in *DMF-DMA* [61]. Since Cu(II) has a distorted octahedral structure with two elongated axial and four shortened equatorial solvent molecules, replacement of one solvent with another occurs differently at the axial and equatorial positions, the latter showing a stronger ion-solvent bonding than the former. According to their result, *DMF* is preferentially solvated at the equatorial position, whereas *DMF* less favorably solvates Cu(II) than *DMA* at the axial position, where less steric hindrance among solvated molecules is expected. In the average, *DMF* is preferentially solvated with Cu(II) in *DMF-DMA* mixtures (Fig. 9).

Concluding Remarks

The study of ionic solvation is traditional but still modern, and it is one of the most fundamental subjects in solution chemistry. The extension of studies in aqueous solution to nonaqueous and mixed solvents leads to a widened view for chemistry in aqueous solution itself. Expansion of solvent composition from single-component to

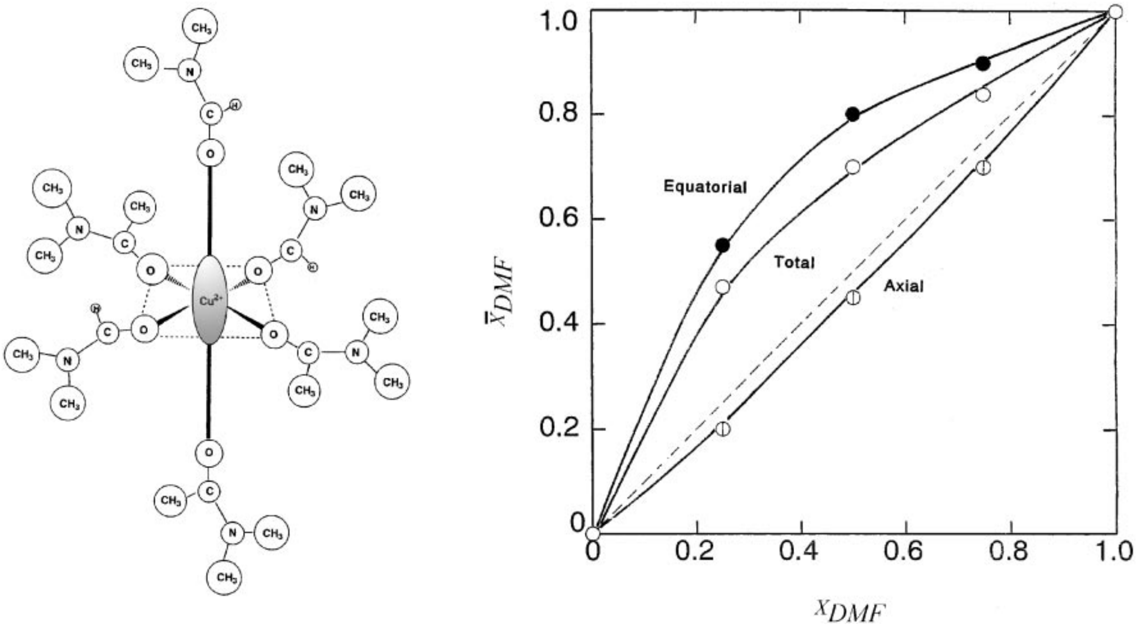


Fig. 9. Preferential solvation of the Cu(II) ion in *DMF-DMA* mixtures; (a): a structural model of a mixed solvated, distorted octahedral Cu(II) ion; (b): plots of $\bar{x}_{DMF}$ *vs.* x_{DMF} for the total composition of Cu(II), solvent composition at the equatorial and axial positions of the Cu(II) ion; quoted from Ref. [61]

multi-component systems brings new interesting results. Ionic solvation is a subject of not only solution chemistry but also analytical chemistry, physical chemistry, electrochemistry, and even industrial and environmental chemistry. Studies on ionic solvation should be much more deeply investigated over wide ranges of temperature, pressure, and solvent composition in the future to present interesting results.

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