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INTRODUCTION

1.1 THE SIGNIFICANCE AND PHENOMENOLOGY OF IONS IN SOLUTION

Chemistry is for a large part conducted in solutions involving ions and such solutions are ubiquitous in nature. Oceans are vast aqueous solutions of salts, consisting mainly of sodium chloride, but other salts and minor components are also present in ocean water. Lakes, rivers, and brackish water are dilute solutions of ions and are essential to survival, since they provide drinking water and water for irrigation. Rain and other precipitates may remove ionic species from the atmosphere that arrived there as spray from oceans and seas or from human activities, for example, acid rain. Physiological fluids consist mostly of water in which colloidal substances, but also ions essential to their function, are dissolved.

It appears from the above that water is the only medium in which ions play a role, but this picture is too narrow because human endeavors utilize many other liquid media in which ions are present and have an active role. The manufacture of organic substances, as raw materials or intermediates in many industries, such as textiles, drugs, and food additives, generally involves reactions carried out in mixed aqueous-organic or completely nonaqueous liquid media in which ions participate. In chemical analysis, such media have long been of invaluable use, for instance in electroanalytical measurements or chromatographic separations. Industrial uses of nonaqueous media involving ions include solvent extraction in hydrometallurgy or in nuclear fuel reprocessing and nuclear waste disposal (Chapter 8).

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The ions involved in these as well as other systems and applications interact with each other and with nonionized solutes that may be present. These interactions are of prime interest to the chemist, but the extent, intensity, and rate of proceeding of these interactions depend heavily on the solvent or solvent mixture present, a fact that is not always clearly recognized by the operator. The ion–solvent interactions should be understood in order to make the best use of the solutions of the ions, since it is the solvated ions that take part in the interactions of interest. If a free choice of the solvent or the solvent mixture to be used is possible, the most suitable one for the purpose should be selected on the basis of the knowledge available on the interactions that take place, bearing in mind also costs, ecology, and hazards. If the solvent is prescribed, this knowledge is still needed in order to select the proper reaction conditions or the additives that could be useful. So-called “bare” or nonsolvated ions occur in gas-phase reactions (Chapter 2) but not in condensed media, that is, in solutions. A seeming exception to this generalization is the use of room temperature ionic liquids (RTILs) as reaction media, where all the ions are surrounded by ions of the opposite charge sign rather than by a nonionic liquid medium. Whether the ions of RTILs are called “bare” or “solvated” is a semantic question. In common situations, which are the subject of this book, there is always an excess of a nonionic liquid medium in which the ions find themselves, the molecules of which surround the ions more or less completely, unless some other species, be it another ion (of opposite sign) or a solute molecule (a ligand) replaces some of the solvent molecules in the ionic solvation shell.

Ions cannot be added individually to any major extent to a solvent or a solution; it is always an electrolyte consisting of ions of both signs in a combination that makes the electrolyte electrically neutral, which is added to form a solution involving ions. Many commonly used and studied electrolytes are crystalline solids, such as NaCl or $(C_4H_9)_4NClO_4$. The electrostatic energy that holds the ions constituting such crystals together, the lattice energy that must be invested in order to separate the ions in the solution, is compensated by the solvation energy that is gained in the process of dissolution, with some effect also of the entropic changes encountered in the process. Some potential electrolytes are gaseous, for example, HCl, but they produce ions only on reaction with the solvent in which the covalent H–Cl bonds are broken and replaced with others to compensate for the energy involved. On the other hand, ions may leave the solution, if not individually then as a small combination of ions, in electrospray experiments, in which they are then monitored in the gas phase by mass spectrometry. The results of such experiments have some bearing on the state of the liquid ionic solutions, but this subject is outside the scope of this book.

It should be kept in mind that, connected with such ion solvation reactions with crystalline or gaseous electrolytes, a further reaction takes place, which is not always recognized, namely the breaking of some solvent–solvent molecular interactions, required to produce the space to accommodate the ions in the solution. It is the balance of all the (Gibbs) energies that have to be invested and those that are gained that determine the extent to which an electrolyte will dissolve in a given solvent (Chapter 4).

Some electrolytes are completely dissociated into "free," that is, solvated, positively charged cations, and negatively charged anions. Other electrolytes are only partly so dissociated, depending on the concentration and on the nature of the solvent. Some substances are ionogenic, in the sense that some dissociation into ions occurs only under specific conditions, and these include also so-called "weak electrolytes" such as many acids and essentially basic substances in aqueous solutions.

A solution of a single, individual ion in a very large amount of solvent could presumably be the basis of a study of ion solvation which is not encumbered by other interactions. This situation cannot be achieved in the laboratory but can be dealt with as a thought process and now for many years also in computer simulations. The results of the latter have by now consolidated into a large body of knowledge that is constantly not only extended but also improved by the level of sophistication that can nowadays be achieved in such simulations. Such results are incorporated into the discussions in the present book, where they are compared with laboratory experimental data obtained on electrolytes, extrapolated to infinite dilution (Chapters 4 and 5). At such high dilutions, each ion is surrounded by solvent molecules only and does not interact with the very remote ions of the opposite charge sign that must be present somewhere in the solution. Still, the allocation of the extrapolated values of the electrolyte properties to its constituent individual ions is a problem that must be solved.

For the purpose of only reducing the number of items in the properties list from the many electrolytes (combination of cations and anions), that have been derived at infinite dilution to the much smaller number of individual ions that constitute them, it is sufficient to employ the so-called "conventional" values. These are based on assigning to one ion, say the solvated hydrogen ion, an arbitrary value (generally zero) and rely on the additivity of individual infinite dilution ionic values to derive values of all other ions. The sum of the conventional ionic values, weighted according to the stoichiometric coefficients (the numbers of ions of each kind constituting the electrolyte), expresses correctly the infinite dilution property of the electrolyte. Within a given charge sign series of ions, say cations only, comparisons between conventional values of diverse ions can throw some light on the effects of the individual ionic properties, such as size and valency, but the cation and the anion series cannot be compared with each other.

The problem of assignment of the so-called "absolute" individual ionic values to these infinite dilution electrolyte data is solved mainly on the basis of chemical intuition (Chapter 4) that can be assisted by the results from computer simulations. Once individual ionic values of their properties in a given solvent (or solvent mixture) at a given thermodynamic state [temperature and pressure, usually specified as 298.15 K (25°C) and 0.1 MPa (less commonly now 1 atm = 0.101325 MPa)] have been established, they may be compared with other properties of the ions (e.g., their sizes) or with theoretical expectations (models). The latter are the main incentives to obtaining the absolute values. Such comparisons and correlations provide insights into the ion–solvent interactions that take place and form the basis for understanding interactions of ions with other solutes, be they ionic themselves or nonionic.

There are some experimental measurements that can be made on solutions of ions that pertain directly to individual ions. These include transport properties, such as the ionic conductivities that are obtained from specific conductivities of electrolytes in conjunction with transport number measurements. Diffusivities of individual ionic species can also be measured by the use of isotopically labeled ions and should be compatible with the mobilities deduced from the ionic conductivities. Spectroscopic data can also in certain cases be due to individual ionic species, such as NMR chemical shifts and relaxation rates of the signals from appropriate nuclei (e.g., ^{7}Li or ^{27}Al). Such information may be used as a guide for the "chemical intuition" mentioned earlier needed for obtaining absolute individual ionic values from measurements on electrolytes extrapolated to infinite dilution.

As already mentioned at the beginning, nonaqueous and mixed aqueous-organic solvents play important roles in chemistry, but water is still the most studied solvent for ions, not only at ambient conditions but also under diverse conditions of temperature, pressure, and the existence of external fields, such as electrical ones. Their solvation by water and their properties in aqueous solutions are therefore useful as a reference basis for evaluation of the effects occurring on the exchange of the water, in part or completely, by another solvent. The situation is complicated by the fact that water is a unique solvent in many respects, and effects encountered in aqueous solutions of ions may be absent in other media. For instance, the effects that ions have on the hydrogen-bonded structure of water, breaking it or enhancing it, have no counterpart in most other solvents, but there are exceptions. The so called "hydrophobic interactions" applicable to ionic species with extended alkyl chains or aromatic rings are practically unique for aqueous solutions. These interactions do not allude only to "model" ions such as $(C_4H_9)_4N^+$ but more importantly to biomolecules in general and specifically also to side chains of proteins that are ionized due to the $–CO_2^-$ or $–NH_3^+$ groups that they carry.

The ion solvation efficacy of nonaqueous solvents, alone or mixed with water, has beneficial results for some uses, such as enhancement of the solubility of ionic substances, but may be detrimental in other aspects, for example, in the availability of ions as reaction partners. Poorly solvated ions are more reactive than strongly solvated ones and this is manifested in the rates of organic reactions. Aprotic solvents (such that do not provide hydrogen bonding) have been found as optimal media for reactions involving anions that are only poorly solvated by them. Nonpolar solvents, on the other hand, have a low solvating power for the ions and therefore play a very minor role in solutions of ions, because of the low solubility of electrolytes in such solvents. Polar solvents, whether protic or aprotic, interact with ions of both charge signs by means of their dipole moments. Protic solvents carry a hydrogen atom capable of hydrogen-bonding to anions whereas both protic and aprotic ones provide a pair of nonbonded electrons to form coordinate bonds with mainly the cations (Chapter 3). The electron pair donor–acceptor properties of the solvents are generally of more importance than the dipole moments of their molecules. The permittivity of the solvent, important for the ionic dissociation of the electrolytes, plays a minor role in the solvation of the ions or properties of the solvated ions, once formed in the solution.

Mixture of solvents poses additional problems to the study of ion solvation and the properties of the solvated ions: the interactions between the molecules of the different solvents with each other besides those of molecules of each solvent among themselves are significant. Also, the selective solvation of the ions by the molecules of the component solvents may affect the solvated ions profoundly: the ions may “see” around them nearly only molecules of the favored component (selective solvation). The preferential solvation of ions in solvent mixture needs to be described quantitatively, and once this is done should be explained in terms of both the solvating properties of the solvents and the properties of the ions (Chapter 6).

Much emphasize has been provided in this introduction to solution of electrolytes at infinite dilution, where individual ionic properties are manifested and may be obtained and discussed. However, “real life” encounters solutions of ions that involve finite, sometimes quite large, concentrations of ions, where interactions of the ions among themselves are important. The number of solvent molecules per formula unit of the electrolyte diminishes with increasing concentrations, and hence the integrity of the ionic solvation shells is eventually broken. The ion–ion interactions then compete with the ion–solvent interactions. Ion pairs, consisting of couples of ions of opposite charge sign, may have transient existence, but an equilibrium concentration of them may result and needs to be taken into account. Similarly, the presence of non-ionic solutes (already referred to earlier text, where solvent mixtures are considered), which may be solid, liquid, or gaseous solutes, poses new forms of interactions that have to be dealt with (Chapter 7).

Several aspects of ion solvation and the properties of solvated ions are dealt with in this introduction. On the whole, one goal of the discussion of ion solvation is the provision of small sets of properties of the ions and of the solvents, from which the solvation can be predicted for any ion/solvent combination. This has been attempted in this book, with a view to be useful for the many applications of ions in solution, examples of which are shown in Chapter 8, with no attempt to exhaust this subject.

1.2 LIST OF SYMBOLS AND ABBREVIATIONS

Chemical species and units of physical quantities are denoted by Roman type characters, whereas physical quantities that can be expressed by numerical values are denoted by Greek or *italic* characters. Mathematical symbols have their usual meaning and are not listed here. The same symbol is used for an extensive property of a system and for the molar quantity of a constituent of the system. The SI system of physical units is used throughout, but some extra SI units commonly used in the physicochemical literature are also included where they simplify the notation. These include the symbols °C for centigrade temperatures ($T/\mathrm{K} - 273.15$), M for $\mathrm{mol{\cdot}dm^{-3}}$, and m for $\mathrm{mol\ (kg{\cdot}solvent)^{-1}}$.

PRINCIPAL LATIN CHARACTERS

A^{z-}	a generalized anion
A	coefficient in the Debye–Hückel expression for activity coefficients
AN	acceptor number of a solvent
a	distance of closest approach of ions in solution (nm)

a_X	thermodynamic activity of species X
(aq)	an ion in aqueous solution, generally at infinite dilution
B	coefficient in the Debye–Hückel expression for activity coefficients
B_η	B-coefficient of the Jones–Dole viscosity expression (M^{-1})
b	coefficient of the expression of the electric field dependence of the permittivity
b	parameter in the Bjerrum expression for ion pairing
C^{z+}	a generalized cation
C_P	molar heat capacity at constant pressure ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)
c_X	molar concentration of species X (M)
(cr)	crystalline phase
D	Debye unit of dipole moments ($3.33564 \times 10^{-30}\,\mathrm{C{\cdot}m}$)
D	diffusion coefficient ($\mathrm{m^2{\cdot}s^{-1}{\cdot}mol^{-1}}$)
DN	donor number of a solvent
d	interatomic distance (nm)
E	generalized electrolyte
E	energy, molar energy ($\mathrm{J{\cdot}mol^{-1}}$)
E	electric field strength ($\mathrm{V{\cdot}m^{-1}}$)
E	electromotive force of an electrochemical cell (V)
E_j	liquid junction potential
E_T	polarity index of a solvent ($\mathrm{kca{\cdot}mol^{-1}}$, $1\,\mathrm{cal} = 4.184\,\mathrm{J}$)
e	elementary charge ($1.6022 \times 10^{-19}\,\mathrm{C}$)
F	Faraday constant ($9.6485 \times 10^{4}\,\mathrm{C\,mol^{-1}}$)
f_X	fraction of species X
G	Gibbs energy, molar Gibbs energy ($\mathrm{J{\cdot}mol^{-1}}$)
g	Kirkwood dipole orientation parameter
(g)	gas phase
$g(r)$	pair correlation function
H	enthalpy, molar enthalpy ($\mathrm{J{\cdot}mol^{-1}}$)
h	solvation (hydration) number
$\mathrm{I}^{z\pm}$	generalized ion
I	ionic strength (M or m)
K	equilibrium constant
K_a, K_b	acid, base dissociation constant in aqueous solutions
K_ass	ion pair association constant (M)
K_W	ion product of water (M^2)
k_B	Boltzmann constant ($1.3807 \times 10^{-23}\,\mathrm{J{\cdot}K^{-1}}$)
k	rate constant of specified reaction (s^{-1} for unimolecular reactions, $\mathrm{M^{-1}{\cdot}s^{-1}}$ for bimolecular reactions)
(l)	liquid phase
M^{z+}	metal ion of charge $z+$
M_X	molar mass of species X (in $\mathrm{kg{\cdot}mol^{-1}}$)
m_X	molal concentration of species X (m)
N	generalized nonelectrolyte solute
N_A	Avogadro's number ($6.0221 \times 10^{23}\,\mathrm{mol^{-1}}$)

N_X	number of particles of species X in the system
n_C	number of carbon atoms in an alkyl chain
n_D	refractive index at the sodium D line
n_X	amount of substance of species X (in mol)
P	pressure (Pa)
p	vapor pressure (Pa)
$Q(b)$	integral in the Bjerrum theory of ion pairing
R	gas constant ($8.3145\,\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)
R_X	molar refractivity of species X ($\mathrm{m^3{\cdot}mol^{-1}}$)
r_X	radius of a particle of species X
S	generalized solvent
S	entropy, molar entropy ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)
$S(k)$	structure factor in k space
s_X	molar solubility of species X (M)
(s)	solid phase
T	temperature (in K)
t	centigrade temperature (°C)
t_b	normal boiling point of liquid (°C at 0.101325 MPa)
t_m	melting (freezing) temperature (°C)
U	Potential interaction energy in the system (J)
u	speed of sound in a liquid ($\mathrm{m{\cdot}s^{-1}}$)
V	volume, molar volume ($\mathrm{m^3{\cdot}mol^{-1}}$)
W	water, a generalized reference solvent
w_X	mass fraction of species X
X	generalized solute
x_X	mole fraction of species X
Y	generalized molar thermodynamic quantity (G, H, S, V, …)
y	packing fraction of a solvent
y_X	molar activity coefficient of species X
Z	lattice parameter
z_X	charge number of ionic species X (taken algebraically)

PRINCIPAL GREEK CHARACTERS

α	fraction of electrolyte dissociated into ions
α	Kamlet–Taft hydrogen bond donation ability of solvent
α_P	isobaric thermal expansibility ($\mathrm{K^{-1}}$)
α_X	polarizability of species X ($\mathrm{m^{-3}}$)
β	Kamlet–Taft electron pair donation ability of solvent
$\gamma_\pm$	mean ionic molal activity coefficient of electrolyte
δ	chemical shift of NMR signal (ppm)
δ_H	Hildebrand Solubility Parameter (in $\mathrm{Pa^{1/2}}$)
ε_0	permittivity of empty space ($8.8542\times10^{-12}\,\mathrm{C^2{\cdot}J^{-1}{\cdot}m^{-1}}$)
ε	relative permittivity

η	dynamic viscosity (Pa·s)
κ	specific conductance ($\mathrm{S{\cdot}m^{-1}}$)
κ_S, κ_T	adiabatic (isentropic), isothermal compressibility ($\mathrm{Pa^{-1}}$)
Λ_E	molar conductivity of an electrolyte E ($\mathrm{S{\cdot}m^{-1}{\cdot}dm^3{\cdot}mol^{-1}}$)
λ_I	molar conductivity of ion I ($\mathrm{S{\cdot}m^{-1}{\cdot}dm^3{\cdot}mol^{-1}}$)
μ	dipole moment (D)
μ_X	chemical potential of species X ($\mathrm{J{\cdot}mol^{-1}}$)
ν	wave number ($\mathrm{cm^{-1}}$)
ν	stoichiometric coefficient (number of ions per formula)
π^*	Kamlet–Taft polarity/polarizability of solvent
ρ	density ($\mathrm{kg{\cdot}m^{-3}}$)
σ	surface tension ($\mathrm{N{\cdot}m^{-1}}$)
σ	molecular collision diameter (nm)
τ	relaxation time, mean residence time (s)
φ_X	volume fraction of species X
χ	molar (diamagnetic) susceptibility ($\mathrm{m^3{\cdot}mol^{-1}}$)
χ	surface potential of a liquid against another phase (V)
ω	frequency of an electromagnetic wave ($\mathrm{s^{-1}}$)

PRINCIPAL SUBSCRIPTS

ad	pertaining to the process of adsorption
cav	pertaining to cavity formation
dip	contribution from dipole interactions
disp	contribution from dispersion interactions
E	pertaining to an electrolyte
el	contribution from electrostatic interactions
els	contribution from electrostriction
f	pertaining to the process of formation
hyd	pertaining to hydration
I	pertaining to the ion I
intr	intrinsic value of solute
neut	pertaining to a neutral species
S	pertaining to the solvent S
soln	for the process of dissolution
solv	for the process of solvation
str	structural contribution
tr	of transfer
vdW	van der Waals radius or volume

PRINCIPAL SUPERSCRIPTS

conv	conventional
E	excess extensive property
F	of fusion

$^{\mathrm{L}}$	local
$^{\mathrm{N}}$	normalized
$^{\mathrm{V}}$	of vaporization
*	standard state of a pure substance
$^{\mathrm{o}}$	standard thermodynamic function
$^{\infty}$	standard state of infinite dilution
$^{\neq}$	of activation
$^{\varphi}$	(presuperscript) apparent molar

A chemical substance or ion is generally referred to in the text by its name or formula, but in tables and as subscripts, abbreviations are generally employed. The common abbreviations of alkyl chains employed are as follows: Me, methyl; Et, ethyl; Pr, 1-propyl; Bu, 1-butyl; Pe, 1-pentyl; Hx, 1-hexyl; Oc, 1-octyl; and Ph, phenyl. Common solvents have the following abbreviations: EG, 1,2-ethanediol; THF, tetrahydrofuran; Diox, 1,4-dioxane; PC, propylene carbonate; FA, formamide; DMF, *N,N*-dimethylformamide; NMPy, *N*-methyl-2-pyrrolidinone; Py, pyridine; DMSO, dimethylsulfoxide; TMS, tetramethylenesulfone (sulfolane), and HMPT, hexamethyl phosphoric triamide. The names of other solvents are occasionally abbreviated as noted in the footnotes of tables.