Chapter 2
Ions

Ions, defined as particles that carry electrical charges, exist in condensed phases (solids and liquids) as electrically neutral combinations of cations and anions: electrolytes. The ions may be bound or relatively free to migrate. Ions may be monatomic, such as K^+or Cl^-, they may consist of a few atoms, such as ammonium, $NH_4{}^+$, or sulfate, $SO_4{}^{2-}$, or even considerably more than a few, such as nitrobenzoate, $O_2NC_6H_4CO_2{}^-$, or tetrapropylammonium, $(C_3H_7)_4N^+$. They may even consist of very many atoms and may carry many dispersed charges and are then referred to as poly-ions, constituting the dissociated part of polyelectrolytes. Some biological moieties, such as polypeptides, proteins, and nucleic acids, as well as suitable synthetic molecules are examples of polyelectrolytes.

The treatment in the following deals mostly with ions in solution, though some discussion of isolated ions is also required. In dilute solutions strong electrolytes, such as NaCl, are those that are fully dissociated into their constituent ions, though they may associate to ion pairs in more concentrated ones, e.g., Na_2SO_4, forming $Na^+ + NaSO_4{}^-$. Weak electrolytes are hardly at all dissociated into ions in solution, but have the capability of doing so under special circumstances. They are ionogenic, that is, capable of ionizing by reaction with some component of the solution, including the solvent itself. A weak acid, such as benzoic acid, C_6H_5COOH, may donate a hydrogen ion to a basic environment and turn into an anion, $C_6H_5CO_2{}^-$. A weak base, such as aniline, $C_6H_5NH_2$, may add-on a hydrogen ion in an acidic medium and turn into a cation, anilinium, $C_6H_5NH_3{}^+$. Zwitterions may turn into anions or cations, depending on the pH of the medium, an example being alanine:$^+H_3NCH(CH_3)COO^-$, turning into$^+H_3NCH(CH_3)COOH$ in acidic media and into $H_2NCH(CH_3)COO^-$ in basic ones. The properties discussed in this chapter pertain to the ions that have been formed, either by strong electrolytes directly on their dissolution or by weak electrolytes in suitable media.

The generalized symbol of an ion (but not of a poly-ion) of any charge sign is $I^{z\pm}$, with an integral charge number z. As a part of the symbol for a quantity pertaining to an ion the subscript $_I$ is used without the charge. As a part of the symbol for a quantity pertaining to an electrolyte or to a neutral combination of ions the subscript $_E$ is used. Subscripts $_+$ and $_-$ represent generalized cations and anions with no regard to z.

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2.1 The Properties of Isolated Ions

When an ion exists in an ideal gaseous state, that is, when it is devoid of interactions with other particles or its surroundings in general, it is termed an isolated ion. Commonly, isolated ions consist of relatively few atoms, but some quite large ones are produced in mass spectrometers. They may also be the centers of clusters consisting of the ion proper surrounded by a small number of solvent molecules.

The ionization process leading from an atom, a radical, or a molecule to a cation may proceed in several stages of losing an electron. It requires the investment of energy and is expressed by the ionization potential, $\sum I_p$, the sum being over the successive ionization stages. The electron capture by an atom, a radical, or a molecule to form an anion releases energy that is expressed as the electron affinity, *EA*, of such a moiety. However, the capture of an electron by an anion that already carries a negative charge is an unlikely event. Therefore, only a single electron may generally be added to a neutral species in the *EA* process. These energies, $\sum I_p$ and *EA*, in electron-volt units (1 eV/particle = 96.483 kJ mol^{-1}), have been reported for many ions in the book by Marcus (1997).

The primary characteristics of isolated ions are the amount of electrical charge they carry, their mass, their shape, and their size. The amount of charge is given in terms of a multiple, z_I, of the elementary units of the charge of a proton (positive) or an electron (negative), namely $e = 1.60218 \times 10^{-19}$ C. Within the scope of this book the absolute values of z_I for isolated ions range from 1 to 4 for monatomic ones and possibly somewhat larger for some complex ions. Highly ionized atoms that may be produced artificially or result from nuclear reactions are not considered here.

The masses of ions are generally specified as their molar mass, that is, of Avogadro's number, $N_A = 6.02214 \times 10^{23}$ mol^{-1}, of ions. The units of the molar mass, M_I, are therefore kg mol^{-1}, but generally M_I is given in g mol^{-1}.

The shape of monatomic ions is, of course, strictly spherical when isolated, but they may be deformed slightly by external forces (strong electrical fields). Ions that consist of several atoms may have any shape, but common ones are planar (NO_3^-, CO_3^{2-}), tetrahedral (NH_4^+, SO_4^{2-}), octahedral ($Fe(CN)_6^{4-}$), elongated (SCN^-), or more irregular ($CH_3CO_2^-$, HCO_3^-).

The sizes of ions in the isolated state, however, are difficult to specify, because the electrons in their periphery extend indefinitely around the inner electronic shells and the nuclei of the atoms. The sizes of monatomic ions may be compared with the iso-electronic noble gases (of known collision diameters), e.g., $O^{2-} > F^- > Ne > Na^+ > Mg^{2+}$. The sizes are expected to diminish in this series, because of the increasing positive nuclear charge that pulls-in the electrons. Stokes (1964) took up this idea with the quantum mechanical scaling principle, and calculated radii for isolated monatomic ions, $r_I^g = r(I^{z\pm}, g)$. These were then used to calculate the self-energy of the ions, used for the estimation of their Gibbs energies of hydration, see Sect. 2.3.3. However, such values of r_I^g have not been taken up by other investigators since then.

The self-energy of an isolated ion ($I^{z\pm}$, g) is due to its being charged and is

$$E_{\text{self}}(I^{z\pm}, g) = \frac{N_A z^2 e^2}{4\pi\varepsilon_0 r_I^g} \tag{2.1}$$

per mole of isolated ions. Here $\varepsilon_0 = 8.85419 \times 10^{-12} C^2\,J^{-1}m^{-1}$ is the permittivity of free space, and r_I^g is the radius of the ion. As stated above, the size of an isolated ion is an ill defined quantity, so must be its radius, hence the self-energy.

On the other hand, thermodynamic quantities that pertain to the formation of isolated ions from the elements in their standard states are well defined. The standard molar Gibbs energy and the enthalpy of formation, $\Delta_f G^\circ(I^{z\pm}, g)$ and $\Delta_f H^\circ(I^{z\pm}, g)$, of many ions have been reported. The standard molar entropy and constant-pressure heat capacity, $S^\circ(I^{z\pm}, g)$ and $C_P^\circ(I^{z\pm}, g)$, of isolated ions are also well defined quantities and have been reported. Such data are generally available for the standard temperature $T^\circ = 298.15$ K and pressure $P^\circ = 100$ kPa, and suitable sources are the NBS tables (Wagman et al. 1982) and the book by Marcus (1997). The standard molar volume of an isolated ion is trivial, being the same for all ions: $V^\circ(I^{z\pm}, g) = RT^\circ/P^\circ = 0.02479\,m^3\,mol^{-1}$, where $R = 8.31451\,J\,K^{-1}\,mol^{-1}$ is the gas constant.

Most ions are diamagnetic, that is, they are repulsed out from a magnetic field; their molar magnetic susceptibilities, χ_{Im}, range from a few to several tens of the unit (-10^{-12} m^3 mol^{-1}), as reported in (Marcus 1997). Ions that have one or more unpaired electrons in their electronic shells are paramagnetic and are attracted into a magnetic field. For a paramagnetic ion having n unpaired electrons $\chi_{Im} = +1.676n(n+2) \times 10^{-9}$ m^3 mol^{-1} at $T^\circ = 298.15$ K. Molar magnetic susceptibilities, thus, have the dimensions of molar volumes.

The polarizibility, α_I, of an ion also has the dimension of a volume, of the order of 10^{-30} m^3 per ion. The molar refractivity (at infinite frequency) is proportional to the polarizability:

$$R_{I\infty} = \left(\frac{4\pi N_A}{3}\right)\alpha_I = 2.5227 \times 10^{24}\alpha_I \tag{2.2}$$

The molar refractivity is obtained experimentally for neutral species, and generally the refractive index at the sodium D line (589 nm), n_D, is used to obtain the molar refractivity R_D in lieu of the infinite wavelength value R_∞. The Lorenz-Lorentz expression is used:

$$R_D = \frac{V(n_D{}^2 - 1)}{n_D{}^2 + 2} \tag{2.3}$$

where $V = (M/\rho)$ is the molar volume and M and ρ are the molar mass and the density. The molar refractivities are not very sensitive to the environment in which an ion is situate (in a condensed phase) nor to its concentration (when in solution). In order to ascribe a molar refractivity (and a polarizability) to an individual ion, the experimental values must be split appropriately between the cation and the anion.

There is no theoretically valid way to do this, so an empirical expedient is resorted to, namely $R_D(Na^+) = 0.65\,cm^3\ mol^{-1}$ at 25 °C (Heydweiler 1925). The temperature coefficient of R_D is rather small, approximately $+0.01\,cm^3\ mol^{-1}$.

A mild correlation of the polarizabilities exists with the 'softness' that can be ascribed to the ions. The softness is related to the difference between the energetics of formation of the ion from the neutral species on the one hand (loss or gain of electrons) and its enthalpy of hydration (Sect. 2.3.1) on the other. In the hydration process the charge on the ion itself is neutralized to some extent by the gain or loss of pairs of electrons by coordination with the solvent. The softness parameter was given normalized numerical values by Marcus (1986), for cations according to:

$$\sigma_+ = \frac{\frac{\sum I_p + \Delta_{hydr}H^\infty(C^{z+})}{z_+} - I_p(H^+) + \Delta_{hydr}H^\infty(H^+)}{I_p(H^+) + \Delta_{hydr}H^\infty(H^+)} \tag{2.4}$$

and for anions according to:

$$\sigma_- = \frac{\frac{-EA - \Delta_{hydr}H^\infty(A^{z-})}{z_-} - (EA(H)) - \Delta_{hydr}H^\infty(OH^-)}{-EA(H) - \Delta_{hydr}H^\infty(OH^-)} \tag{2.5}$$

The aqueous hydrogen and hydroxide ions are arbitrarily assigned softness values of zero and the dimensionless values for cations and anions are then related to these values. They have been listed for many ions (Marcus 1986, 1977); positive values of the softness parameter denote 'soft' ions and negative values denote 'hard' ions. As said, for soft ions there is some correlation with their polarizabilities but for hard ions the correlation is much better with the electric field strength, $z_1 e/r_1^2$, instead.

The properties of a selected list of ions in the isolated state are shown in Table 2.1.

2.2 The Properties of Aqueous Ions

The electrostatic interactions of the cations and anions making up an electrolyte in aqueous solutions compete with the thermal movement of all the particles in the solution, ions and water molecules, and are screened by the high dielectric permittivity of the water. The overall interactions, involving ion hydration and effects of ions on the water structure, in addition to ion-ion interactions and those of the hydrogen bonded network of water, are quite complicated. Approximations have to be applied in order to handle the resulting behavior of the ions theoretically or by means of computer simulations.

The simplest approximation is the '*restricted primitive model*' that considers the ions as charged conducting spheres dispersed uniformly in a continuum fluid made up of a compressible dielectric. The ions are characterized by their charges (sign and magnitude) and sizes (radii), and are assumed to be spherical. The solvent, whether single or a mixture, is characterized by its permittivity, compressibility, and

Table 2.1 Properties of some isolated ions (Marcus 1997)

Ion	z	M_I (g mol^{-1})	$\Delta_f H_I^\circ$ (kJ mol^{-1})	$\Delta_f G_I^\circ$ (kJ mol^{-1})	S_I° (J K^{-1} mol^{-1})	C_{pI}° (J K^{-1}mol^{-1})	$\sum I_p/EA$ (eV)	$\chi_{mI} - 10^{-12}$ (m^3 mol^{-1})	$R_{DI}10^{-6}$ (m^3 mol^{-1})	σ_+ or σ_-
H^+	1	1.008	1,536.2	1,523.2	108.9	20.8	1,318	−6.6	−0.1	0
Li^+	1	6.94	685.8	685.8	113.0	20.8	526	−3	0.08	−1.02
Na^+	1	22.94	609.4	580.5	148.0	20.8	502	2.3	0.65	−0.60
K^+	1	39.10	514.3	487.3	154.6	20.8	425	11.2	2.71	−0.53
Cs^+	1	132.91	458	433	169.9	20.8	382	34	6.89	−0.54
NH_4^+	1	18.04	630	681	186.3	34.9	458	11.5	4.7	−0.60
$(CH_3)_4N^+$	1	74.15	546	734	331.9	109.6		65	22.9	
Mg^{2+}	2	24.31	2,348.5	2,300.3	148.7	20.8	2,201		−0.7	−0.41
Ca^2	2	40.08	1,925.9	1,892.1	154.9	20.8	1,748	−1	1.59	−0.66
Ba^{2+}	2	137.33	1,660	1,628	170.4	20.8	1,480	21.5	5.17	−0.66
Fe^{2+}	2	55.85	2,749.9	2,689.6	180.3	25.9	2,334	19.6*	2.1	−0.16
Fe^{3+}	3	55.85	5,712.8	5,669.1	174.0	20.8	5,296	15.6*	3.2	0.33
La^{3+}	3	138.91	3,905	3,771	170.5	20.8	3,474	20	2.74	−0.75
F^-	−1	18.99	256	269	145.6	20.8	32.8	13	2.21	−0.66
Cl^-	−1	35.45	−233.1	−241.4	154.4	20.8	−349	28	8.63	−0.09
Br^-	−1	79.91	−219.1	−245.1	163.6	20.8	−324	39	12.24	0.17
I^-	−1	126.91	−197	−230.2	169.4	20.8	−295	57	18.95	0.50
SCN^-	−1	58.08			166.5	43.2	−207	35	17	0.85
NO_3^-	−1	62.01	−320	−272.8	245.2	44.7	−378	23	10.43	0.15
ClO_4^-	−1	99.45	−344	−266.8	263.0	62.0	−454	34	12.77	−0.30
$CH_3CO_2^-$	−1	59.04	−504.2	−464.1	278.7	61.4	326	32.4	13.87	−0.22
HCO_3^-	−1	61.02	−738	−702	257.9	50.6			10.9	
$H_2PO_4^-$	−1	96.99	−1,280	−1,190	286.7	62.5			14.6	
CO_3^{2-}	−2	60.01	−321	−300.9	246.1	44.4	226	34	11.45	−0.50
SO_4^{2-}	−2	96.07	−758	−704.8	363.6	62.4	1,660	40	13.79	−0.38
HPO_4^{2-}	−2	95.98			283.0	67.8				
PO_4^{3-}	−3	94.97			266.4	65.4	−657	50	15.1	−0.78

Paramagnetic ions are marked by *

thermal expansibility. The properties of the aqueous ions may then be estimated by the application of electrostatic theory and compared with the experimental values.

However, there are very few experimental determinations that can be applied unambiguously to individual ions in aqueous solution. Only as a thought process, may a single ion $I^{z\pm}$ be transferred from the ideal gas phase into water, but this process involves the passage through the gas-water interface. Such a passage is connected with not well defined consequences. Once an individual ion is in solution, its properties depend in principle on its location with respect to the surface and the walls of the vessel, due to its electric field. It is assumed that when such a thought process is carried out simultaneously for ions of opposite matching charges, the effects of the passage through the gas-water interface cancel out, so that valid quantities can be derived from the process.

The more common process that can be carried out experimentally is to dissolve in water an entire electrolyte, consisting of a matched number of cations and anions to produce a neutral species. Conditions can be chosen for approximating infinite dilution as a limit of extrapolation from low, finite concentrations. This limit corresponds to the dissolution of an infinitesimal amount of electrolyte in a finite amount of water or a mole of electrolyte in a huge amount of water. It is then possible to deal with the molar quantities pertaining to the aqueous electrolyte at infinite dilution. One must still devise some means to deduce from the measured quantities those pertaining to the individual ions.

At infinite dilution each ion is surrounded by solvent molecules only and is remote from other ions and does not interact with them. The individual ionic quantities contributing to the measured molar properties of the infinitely dilute electrolyte are, therefore, additive. They are weighted by their stoichiometric coefficients in the electrolyte: ν_+ cations C^{z+} and ν_- anions A^{z-}. For a 1:1 electrolyte such as KBr $\nu_+ = \nu_- = z_+ = |z_-| = 1$, for a 1:2 electrolyte such as $CaCl_2$ $\nu_+ = 1, z_+ = 2, \nu_- = 2$ and $|z_-| = 1$. From the additivity follows that if the value for some one ion is known, those of all other ions can be derived by subtraction of this value, appropriately weighted, from the values for electrolytes containing it, and so forth for other electrolytes. So-called '*conventional*' values are obtained when the value zero is assigned to the aqueous hydrogen ion, $Y^\infty(H^+, aq) = 0$ at all temperatures, Y^∞ being any additive property. Sums of appropriately weighted conventional values of cations, ${Y^\infty}_+^{conv}$, and of anions, ${Y^\infty}_-^{conv}$, represent the values for electrolytes, even those not measured directly. Values of ${Y^\infty}_+^{conv}$ of cations can be compared and discussed among themselves, and similarly for anions among themselves, but they may *not* be construed as representing the actual values that individual ions have these properties.

The problem of the validity of methods for obtaining the so-called '*absolute*' property values of individual aqueous ions was discussed by Conway (1978) and more recently by Marcus (2008a) and by Hünenberger and Reif (2010). These issues are treated in the following sections dealing with the properties of aqueous ions.

It is important to bear in mind the consequences of the electric charge on the ion in aqueous solutions. The electric field at the boundary between the ion and its hydration shell is huge, of the order of many GV m^{-1}. For instance, the field right

near the surface of a sodium ion, at 0.102 nm from its center, is 138.4 GV m^{-1}. Such fields surpass many-fold fields achievable experimentally in the laboratory, these being of the order of 1 GV m^{-1}. The two most important consequences of such large fields are a high compressive pressure and dielectric electrostatic saturation at the hydration layers around an ion. The permittivity of water at very high fields is given by the non-linear dielectric effect:

$$\varepsilon_W(E) = \varepsilon_W(0) + \beta E^2 \tag{2.6}$$

with $\beta = -1.080 \times 10^{-15}$ V^{-2} m^2 that is practically temperature-independent at very high fields. Dielectric saturation prevails at a short distance from the center of an ion, $\sim 0.40|z|^{1/2}$ nm, the relative permittivity diminishing to near the optical limit of n_∞^2 (the infinite frequency refractive index squared) $\approx$1.95 at 25 °C. The dipoles of the water molecules can then no longer be oriented by external fields and the residual permittivity is due to the electronic polarization of the water molecules. The other consequence is the large electrostriction produced by the compressive pressure that the field exerts on the water near the ion. Bockris and Saluja (1972) calculated the effective pressure in the middle of the first hydration shell of ions, the numerical coefficient being valid at 25 °C with the radii in nm:

$$\frac{P_{\text{eff}}}{\text{GPa}} = 0.18305(r_I + r_W)^{-3} \tag{2.7}$$

For the sodium ion the pressure is 13.2 GPa at this site, commensurate with the highest experimental pressures that can be applied to water or electrolyte solutions in the laboratory. At such large pressures the water in the hydration shell is highly compressed, it is strongly electrostricted.

2.2.1 Hydration Numbers

A Cation has the water molecules oriented towards it with one of their lone pairs of electrons, carrying a fractional negative charge, pointing at the cation. This may result in a coordinate bond, the fractional charge penetrating an unoccupied electronic orbital of the cation. Small multivalent cations, such as Mg^{2+}, tend to form such bonds with water, with definite coordination geometries and numbers of the water molecules in the first hydration shell: 6 in a regular octahedron for Mg^{2+}. These water molecules are polarized by the charge of the cation and are therefore strongly hydrogen-bond donors to water molecules in a second hydration shell that remains with the cation as it moves in the solution.

An anion in aqueous solutions has the water molecules pointing one (or both in some cases) of their hydrogen atoms towards it, resulting in hydrogen bonds. Anions tend to be large and have a relatively small electric field, and have no definite coordination number of water molecules hydrating them. For singly charged anions the average binding of water molecules is rather small (<2). Multivalent anions,

especially oxyanions, such as CO_3^{2-} or SO_4^{2-} bind more water molecules by accepting hydrogen bonds from them, and anions such as HSO_4^- or $H_2PO_4^-$ also donate hydrogen bonds to adjacent water molecules.

Ions containing hydrophobic parts, such as $C_2H_5CO_2^-$ and $C_6H_5NH_3^+$, arrange water molecules differently around such parts, $-C_2H_5$ and $-C_6H_5$, compared with the arrangement near the hydrophilic part, $-CO_2^-$ or $-NH_3^+$. This behavior is even more characteristic of ionic surfactants with long organic chains, such as $(C_8H_{17})_3NH^+$ or $C_{12}H_{25}OSO_3^-$. These tend to associate in aqueous solutions forming micelles or other structures. Ions with hydrophobic groups in their periphery around a buried charge, such as $(C_6H_5)_4B^-$ or $(C_4H_9)_4N^+$, are generally only poorly hydrated.

Water molecules around ions are arranged in concentric shells: the nearest ones, in the first hydration shell, are relatively strongly bound to the ion and move together with it, as do at least some of the water molecules in a second hydration shell, if present. Large monatomic ions (e.g., Cs^+ and I^-) lack a well-formed second hydration shell. A second shell characterizes multiply charged small ions (e.g., Al^{3+}), the water molecules in it being hydrogen-bonded to those in the first shell more strongly than are the hydrogen bonds in pure water. Large ions with a single charge (e.g., $(C_2H_5)_4N^+$ and larger tetraalkylammonium ions) may not have a hydration shell altogether, but have the water in clathrate-like or enhanced tetrahedral ice-like structures around them as for nonionic hydrophobic solutes. Beyond the hydration shells the water molecules are still affected by the electric field of the ionic charge and the possibility of being hydrogen bonded to the inner water molecules. In this region the hydrogen-bonded structure of the water is less ordered than in pure water (see Sect. 1.1.3). Only further out from the ion does the water become bulk water, having the properties of pure water.

Hydration numbers are the time-average numbers of water molecules residing in the first hydration shells of ions (and in the second, if formed). When coordinate bonds are formed between an ion and water molecules a definite integer (primary) hydration number results, equaling the coordination number, (e.g., 4 for Be^{2+}, 6 for Mg^{2+} and Al^{3+}). If only non-directional electrostatic association takes place, then geometric constraints may occur, smaller ions having smaller hydration numbers than larger ions, although the water molecules are bonded more energetically to the former. Fractional average hydration numbers then reflect the probabilities of the temporary localization of a certain number of water molecules around such ions. There is a dynamic exchange of water molecules with the bulk water outside the hydration shells. Over time, water molecules depart from the hydration shells and others come in, resulting in a non-integer hydration number. The rate of such exchanges may be as large as 10^9 per second when no coordinate bonds are formed (e.g., for Cs^+) and as small as $10^{5.2}$ exchanges per second for Mg^{2+}, and an even much smaller rate for an ion such as Cr^{3+}.

Consideration of hydration numbers requires, of course, departure from the strict primitive model (see p. 52) since it recognizes the molecular nature of the aqueous solvent. This number must be defined operationally, since diverse methods are sensitive in different ways to the number of water molecules in the hydration shells.

In an infinitely dilute solution of an ion in water the electric field of the ion causes compression of the water in its hydration shell, electrostriction. Independently of the nature of the ion, the compression of electrostricted water at 298.15 K per mole of water is $\Delta V_{\mathrm{Welec}} = -2.9\ \mathrm{cm^3\ mol^{-1}}$. This value is obtained from the isothermal compressibility of pure water, κ_{TW}, and the pressure derivative of its relative permittivity, $(\partial \ln \varepsilon / \partial P)_T$ (Marcus 2005, 2009).

The molar electrostriction of the water by an ion at infinite dilution, ${V_{\mathrm{Ielec}}}^{\infty}$, is obtainable from a stepwise, shell-by-shell electrostatic calculation (Marcus and Hefter 1999), see below, Sect. 2.2.2.

The ratio between the molar ionic electrostriction, ${V_{\mathrm{Ielec}}}^{\infty}$, and the molar electrostriction of the water, $\Delta V_{\mathrm{Welec}}$, is:

$$ {h_{\mathrm{Ielec}}}^{\infty} = \frac{{V_{\mathrm{Ielec}}}^{\infty}}{\Delta V_{\mathrm{Welec}}} \tag{2.8} $$

and can be construed to represent the time-average hydration number of the ion.

Alternatively, the ion and the water in its first hydration shell may be considered to be non-compressible by an external pressure, the electric field having already produced the maximal possible compression. Then the hydration number is defined by the standard molar ionic compression, $(\partial {V_{\mathrm{I}}}^{\infty}/\partial P)_T$, as:

$$ {h_{\mathrm{Icomp}}}^{\infty} = 1 - \frac{(\partial {V_{\mathrm{I}}}^{\infty}/\partial P)_T}{\kappa_{\mathrm{TW}} {V_{\mathrm{W}}}^{*}} \tag{2.9} $$

Here $(\partial {V_{\mathrm{I}}}^{\infty}/\partial P)_T$ is a negative quantity. Individual ionic values of $(\partial {V_{\mathrm{I}}}^{\infty}/\partial P)_T$ are obtained from experimental values for electrolytes by assuming a value for one ion. The value $(\partial {V_{\mathrm{I}}}^{\infty}/\partial P)_T(\mathrm{Cl^-,aq}) = -16.5 \pm 1.5\ \mathrm{cm^3\ GPa^{-1}\ mol^{-1}}$ at 298.15 K was suggested (Mathieson and Conway 1974). The hydration numbers from these two methods are shown in Table 2.2 and are compared with the approximation $h_{\mathrm{I}}^{\infty} = 0.360|z|/(r_{\mathrm{I}}/\mathrm{nm})$ (Marcus 1997) (see also the end of Sect. 2.2.5), that can be used for ions for which no other value of the hydration number is available.

Hydration numbers are expected to diminish as the concentration of the electrolyte increases, mildly at low concentrations but strongly when the hydration shells of oppositely charged ions start to overlap. This concentration can be estimated from the average distance between ions in a solution that is inversely proportional to the cube root of the concentration:

$$ d^{\mathrm{av}} = {N_A}^{-1/3}\left(\sum \nu_{\mathrm{I}} c_{\mathrm{I}}\right)^{-1/3} = 1.1844\left(\sum \nu_{\mathrm{I}} c_{\mathrm{I}}\right)^{-1/3}\mathrm{nm} \tag{2.10} $$

The summation extends over all the ions present at concentrations c_{I} in M multiplied by their stoichiometric coefficients ν_{I} (Marcus 2009b). The radius of a hydrated ion, r_{Ihydr}, may be taken as the sum of the ionic radius and the diameter of a water molecule (see below), so that it is possible to estimate the concentration at which the hydration shells start to overlap: $d^{\mathrm{av}} \leq r_{\mathrm{I+hydr}} + r_{\mathrm{I-hydr}}$. It is as low as 1.43 M for aqueous NaCl and is lower still for solutions of unsymmetrical multivalent electrolytes (1:2, etc.). Below the overlap limit experimental values of $(\partial V_{\mathrm{I}}/\partial P)_T$ may be used for the estimation of the hydration numbers at finite concentrations from the expression (2.10) for h_{Icomp} given above.

Table 2.2 Properties of some ions in aqueous solutions at 298.15 K (Marcus 1997)

Ion	r[a] (nm)	V_I^{∞} ($cm^3\ mol^{-1}$)	$V_{Ielec}^{\infty b}$ ($cm^3\ mol^{-1}$)	$h_{Ielec}^{\infty b}$	$h_{Icomp}^{\infty b}$	h_{Imodel}^{∞}	S_I^{∞} ($J\ K^{-1}\ mol^{-1}$)	C_{PI}^{∞} ($J\ K^{-1}\ mol^{-1}$)
H^+	0	−5.4					−22.2	−71
Li^+	0.069	−6.4	−12.9	4.4	4.0	5.2	−8.8	−9
Na^+	0.102	−6.7	−8.6	2.9	4.5	3.5	36.8	−28
K^+	0.138	3.5	−5.9	2.0	3.5	2.6	80.3	−58
Cs^+	0.170	15.8	−4.4	1.4	1.3	2.1	111.3	−94
NH_4^+	0.148	12.4				2.4	74.7	−1
$(CH_3)_4N^+$	0.280	84.1			0.4	1.3	187.8	166
Mg^{2+}	0.072	−32.2	−52.5	11.4[c]	10.0	10.0	−182.5	−158
Ca^2	0.100	−28.9	−38.5	10.0[c]	9.0	7.2	−97.5	−169
Ba^{2+}	0.136	−23.5	−27.5		10.3	5.3	−37.8	−188
Fe^{2+}	0.078	−34.4		(11.8)[c]		9.2	−182.1	−188
Fe^{3+}	0.065	−60.2		(21.1)[c]		16.6	−382.5	−204
La^{3+}	0.105	−55.6			15.1	10.3	−284.2	−339
F^-	0.133	4.3	−6.2	2.1	6.7	2.7	8.4	−45
Cl^-	0.181	23.3	−4.0	1.4	2.0	2.0	78.7	−56
Br^-	0.196	30.2	−3.5	1.2	1.8	1.8	104.6	−60
I^-	0.220	41.7	−2.8	1.0	1.5	1.6	133.5	−50
SCN^-	(0.213)	41.2		0.5[c]	0.1[b]	1.7	166.5	42
NO_3^-	(0.200)	34.5		1.4[c]	0.7[b]	1.8	168.8	−1
ClO_4^-	0.240	49.6	−2.4	0.8		1.5	206.2	46
$CH_3CO_2^-$	(0.232)	46.2			4.0[b]	1.6	108.8	97
HCO_3^-	(0.156)	28.9			1.7[b]	2.3	120.6	18
$H_2PO_4^-$	(0.200)	34.6				1.8	114.7	37
CO_3^{2-}	(0.178)	6.7		(10.9)[c]	14.4[b]	4.0	0.9	−159
SO_4^{2-}	0.230	25.0	−13.8	4.6	10.4[b]	3.1	63.2	−138
HPO_4^-	(0.200)	18.7				3.6	10.9	−102
PO_4^{3-}	0.238	−14.1				4.5	−155.4	−283

[a]Values in parentheses are approximate since ions are not nearly spherical; see text
[b]The values from (Marcus 2009), those in parenthesis are the mean values for ions of the given charge
[c]The values from (Marcus 2005), those in parenthesis are the mean values for ions of the given charge

2.2.2 Ionic Radii in Solution

The distances d_{I-O} between the centers of ions and those of the oxygen atoms of adjacent water molecules have been measured by x-ray and neutron diffraction methods and were summarized by Marcus (1988) and by Ohtaki and Radnai (1993). When the radius of a water molecule, $r_W = 0.138$ nm, is deducted from the d_{I-O} values the results correspond quite well with the set of Pauling radii, r_I^P, of the ions in crystals (Marcus 1983). The electrostatic forces acting on ions in condensed phases, crystals and solutions, are similar and the relevant energies, the lattice energies and energies of solvation, are of similar magnitude. Hence, the conclusion that the r_I^P, derived from measurements on crystals, are relevant for the radii of ions in solution is reasonable. The values of d_{I-O} reported by various authors for aqueous electrolyte solutions and pertaining to different concentrations have a mean uncertainty of ± 0.002 nm, much worse than the values in crystals (Shannon and Prewitt 1969, 1970). Within this uncertainty, the 'selected' (Marcus 1997) ionic radii r_I, listed in Table 2.2, added to r_W do yield the experimental d_{I-O} values, so that they validly represent the radii of aqueous ions.

David and Fourest (1990) challenged the concept of a constant radius for the water molecule, r_W. The electric field of the ions polarizes the water molecules adjacent to them and for multiply charged ions squeezes these molecules somewhat in the direction of the ions. The values of r_W decrease according to these authors from 0.143 nm for the alkali metal cations down to 0.133 nm for the trivalent lanthanide cations. Therefore, using the mean value, $r_W = 0.138$ nm, increases accordingly the uncertainty of the ionic radii in solution from ± 0.002 to ± 0.005 nm.

The radii of multi-atomic ions was estimated as thermochemical radii by Jenkins and co-workers (Jenkins and Thakur 1979; Jenkins et al. 1999; Roobottom et al. 1999) from the lattice potential energies U_{lat} of crystals containing them with a monatomic counter-ion of known radius. The sum of the radii of the cation and anion is:

$$r_{I+} + r_{I-} =$$
$$121.4(\nu_+ + \nu_-)z_+z_-[1 + \{1 - (0.138U_{lat}/121.4(\nu_+ + \nu_-)z_+z_-)\}^{1/2}]/2U_{lat} \quad (2.11)$$

So, if r_{I+} is known r_{I-} is obtained and vice versa.

The temperature dependence of the ionic radii of monatomic- as well as multi-atomic ions is negligible within the temperature range of the existence of water as a liquid at ambient pressures (Krestov 1991).

2.2.3 Ionic Volumes

The volumes that are to be assigned to ions in aqueous solutions are related to the measurable concentration-dependent densities, ρ, of the electrolyte solutions at

constant temperature and pressure. Consider a solution made up from n_W moles of water and n_E moles of electrolyte. The apparent molar volume of the latter:

$$^{\varphi}V_E = \frac{(V - n_W V_W{}^*)}{n_E} \tag{2.12}$$

is that part out of the total volume of the solution, V, remaining for the electrolyte per mole of it, once the volume assigned to the water, $n_W V_W{}^*$, is subtracted. The latter quantity is the volume that the water would have occupied if there was no effect due to the ions. In a solution of density ρ made up from $n_W = 55.51$ moles of water (1 kg) and $n_E = m_E$ moles of electrolyte (i.e., at a molality m_E) the apparent molar volume is obtained from the densities as:

$$^{\varphi}V_E = \frac{M_E}{\rho} + \frac{1000(\rho - \rho_W{}^*)}{\rho \rho_W{}^* m_E} \tag{2.13}$$

where M_E is the molar mass of the solute and $\rho_W{}^*$ the density of pure water. This apparent molar volume of the solute does not mean the actual volume that should be assigned to the electrolyte, because the water near ions does not have the same molar volume that pure water has. The water near the ions is compressed, electrostricted, by the electrical fields of the ions. The volume to be assigned to the ions is the partial molar volume, which for a solution of molality m_E is:

$$V_E = {}^{\varphi}V_E + m_E(\partial {}^{\varphi}V_E/\partial m_E)_T \tag{2.14}$$

Usually the second term of Eq. (2.14) is replaced by $m_E{}^{1/2}(\partial {}^{\varphi}V_E/\partial m_E{}^{1/2})_T$, because of the square root dependence of $^{\varphi}V_E$ on m_E in dilute solutions according to the Debye-Hückel theory. On extrapolation to infinite dilution $^{\varphi}V_E$ becomes equal to the standard partial molar volume of the electrolyte: $^{\varphi}V_E{}^{\infty} = V_E{}^{\infty}$.

At infinite dilution the properties of the cations and anions are additive as mentioned above, so that assuming the value of $V^{\infty}(I^{z\pm}, aq)$ for just one ion permits the splitting of the measured $V_E{}^{\infty}$ to the contributions from the individual ions. Conventional values $V_I{}^{conv}$, based on $V^{\infty}(H^+, aq)^{conv} = 0\,cm^3\,mol^{-1}$ at all temperatures, have been listed by Millero (1971) at several temperatures (0, 25, 50 and 75 °C); some of these values have since been revised (Marcus 2011). The temperature-dependent value for the aqueous hydrogen ion was suggested by Millero (1971), valid to 200 °C:

$$V^{\infty}(H^+, aq)/cm^3 mol^{-1} = -5.1 - 0.008(t/°C) - 1.7 \times 10^{-4}(t/°C)^2 \tag{2.15}$$

resulting in $V^{\infty}(H^+, aq) = -5.4\,cm^3\,mol^{-1}$ at 298.15 K. The derived so-called 'absolute' values are $V^{\infty}(I^{\pm}, aq) = V_I{}^{conv} + z_I V^{\infty}(H^+, aq)$. Those at 298.15 K for some ions are shown in Table 2.2. The steps that have led to Eq. (2.15) cause the ionic values to have uncertainties of at least $\pm 0.2 z_I\ cm^3\ mol^{-1}$, thus increasing with the ionic charges. For some cations, and in particular for multivalent ones, the values of $V^{\infty}(I^{z\pm}, aq)$ are negative: these ions cause a large electrostriction of the hydrating water.

The values of the individual ionic V_I at finite concentrations are not known as accurately, contrary to those at infinite dilution, ${V_I}^\infty$. This is due to interionic interactions causing the additivity of the individual volumes to breaks down. According to Redlich and Meyer (1964) the apparent molar volumes of electrolytes can be expressed as:

$$ {}^\varphi V_E = {}^\varphi {V_E}^\infty + S_V {c_E}^{1/2} + b_E c_E \tag{2.16} $$

where c_E is the molar concentration (in M), S_V is the theoretical slope of the square root term according to the Debye-Hückel theory (1.85 $dm^{3/2}$ $mol^{-1/2}$ at 298.15 K), and b_E is an empirical parameter specific for each electrolyte. Since ${}^\varphi {V_E}^\infty = {V_E}^\infty$ is known from additivity and S_V is independent of the electrolyte, knowledge of the b_E parameters should permit the splitting of measured (Eq. (2.13)) values of ${}^\varphi V_E$ at finite concentrations into the individual ionic contributions. Some progress in this direction was made when it was demonstrated that linear relationships exist between the b_E values and the B_η coefficients of the viscosities (Marcus 2006), the latter being additive and established for individual ions (see Sect. 2.4.3).

The standard partial molar volume of an ion in aqueous solution, ${V_I}^\infty$, is the actual volume to be assigned to the ion in the solution (at infinite dilution). It is the sum of its intrinsic volume, ${V_{IIntr}}^\infty$, and the electrostriction that the ion has caused in the water around it, ${V_{Ielec}}^\infty$, the latter being a negative quantity. The volume of a 'bare' unhydrated ion, $(4\pi N_A/3){r_I}^3$, cannot represent its intrinsic volume and must be enlarged to account for the void spaces between the water molecules and the ion and among themselves in order to represent the intrinsic volume of the ion in the solution. A factor of $k = 1.213$ was proposed by Mukerjee (1961) for the alkali metal and the halide ions, producing:

$$ {V_{I\,Intr}}^\infty = \left(\frac{4\pi N_A}{3} \right) (k r_I)^3 \tag{2.17} $$

The sums of the cation and anion values according to Eq. (2.17) agree with the intrinsic volumes obtained as the limits of V_E at very high concentrations, where all the water present is already completely compressed, so that $V_{Ielec} \to 0$ (Marcus 2010).

The electrostriction caused by an ion has been estimated on the basis of the electrostatic effects the very high electric field of an ion has on the water surrounding it. This field exerts a large pressure on the water and sharply decreases its permittivity, down to dielectric saturation. A stepwise shell-by-shell calculation (Marcus and Hefter 1999) yields the desired quantity:

$$ \begin{aligned} {V_{Ielec}}^\infty = & -(8\pi^2 N_A \varepsilon_0) \sum\nolimits_j (r(j)^3 - r(j-1)^3) \\ & \times \left\{ \varepsilon_W(j) \left[\left(\frac{\partial \ln \varepsilon_W}{\partial P} \right)_T - \kappa_{TW} \right] + \kappa_T \right\} E(j)^2 \end{aligned} \tag{2.18} $$

The summation extends over the shell numbers j from 1 up to such a value that the incremental change in ${V_{Ielec}}^\infty$ is negligible. In expression (2.18) $r(0) = r_I$, $\Delta r =$

$r(j) - r(j-1)$ is fixed at some small value, say 0.005 nm, $\varepsilon_W(j) = \varepsilon(j, E)$ is the electric field-dependent (hence pressure-dependent) relative permittivity in the jth shell, and $E(j) = E(j, \varepsilon_W)$ is the electric field strength in the jth shell. An iterative calculation is required due to the mutual dependence of E and ε_W.

The mutual dependences of the pressure, the compressibility, the permittivity, and the field strength complicate the electrostatic calculations. Marcus has recently calculated (Marcus 2009, 2012a) the ${V_{Ielec}}^{\infty}$ for the alkali metal and alkaline earth metal cations and the halide, perchlorate, and sulfate anions for aqueous solutions at five temperatures between 273.15 and 473.15 K (0 − 200 °C), those for 298.15 K being shown in Table 2.2. The corresponding intrinsic volumes are ${V_{I\ Intr}}^{\infty} = {V_I}^{\infty} - {V_{Ielec}}^{\infty}$, and, of course, all are positive.

2.2.4 *Molar Heat Capacities of Aqueous Ions*

When the heat of solution of an electrolyte in water to form a dilute solution is measured calorimetrically at several temperatures, the standard partial molar (constant pressure) heat capacity of the electrolyte, ${C_{PE}}^{\infty}$, is obtained from the temperature coefficient of these heats, extrapolated to infinite dilution. Alternatively, the difference between the specific heat of a dilute solution of the electrolyte and that of water is obtained by flow microcalorimetry to yield the same quantity. Accurate density data at the appropriate temperature are required for the use of this technique. A recent description of the methods available for the determination of the heat capacities of aqueous electrolytes is presented by Hakin and Bhuiyan (2010). Such determinations are accurate to ± 1 to ± 4 J K^{-1} mol^{-1} (Hepler and Hovey 1996)

Values of ${C_{PE}}^{\infty}$ have been critically compiled by Abraham and Marcus (1986) for many electrolytes. Some of the values have later been revised and supplemented by Criss and Millero (1996, 1999) and by Hepler and Hovey (1996). As for other pertinent quantities, it is necessary to assume a value for one ion in order to obtain the so-called 'absolute' standard molar ionic heat capacities, ${C_{PI}}^{\infty}$, these values being additive at infinite dilution. Criss and Millero (1996, 1999) presented values of the conventional standard molar ionic heat capacities at 298.15 K, based ${C_P}^{\infty}(H^+, aq)^{conv} = 0$. The 'absolute' value ${C_P}^{\infty}(H^+, aq) = -71 \pm 14$ J K^{-1} mol^{-1} at 298.15 K has been suggested (Abraham and Marcus 1986) on the basis of the TPTB assumption, equating the standard molar heat capacities of aqueous tetraphenylphosphonium and tetraphenylborate ions. These cation and anion should have similar values of ${C_{PI}}^{\infty}$, because they are chemically similar and have similar sizes, the charges being buried well inside the tetraphenyl structure (Marcus 1987). However, the ${C_{PI}}^{\infty}$ of these bulky ions are large, leading to a large uncertainty involved in equating them, because of slight differences in their sizes. Unfortunately, no more satisfactory method for splitting ${C_{PE}}^{\infty}$ into the ${C_{PI}}^{\infty}$ of the constituent ions has been found so far. Values of the latter are shown in Table 2.2.

Criss and Millero (1996, 1999) used the Pitzer formulation for activity coefficients (Pitzer and Mayoraga 1973) and presented the needed electrolyte specific parameters

for the calculation of the partial molar heat capacities of electrolyte solutions at appreciable concentrations. Hakin and Bhuiyan (2010) presented the semi-empirical Helgeson et al. (1981) expression for similar calculations, useful in particular for elevated temperatures.

2.2.5 Molar Entropies of Aqueous Ions

The standard molar entropies of aqueous electrolytes, S_E^∞, are obtained from the temperature coefficients of the electromotive forces of galvanic cells or of the solubilities of sparingly soluble salts. The values for individual ions need an assumption concerning the value of one ion, as in the cases of the standard molar volumes and heat capacities. The standard molar entropy of the hydrogen ion $S^\infty(H^+, aq)$ can be obtained from from thermocells or from the potential of a mercury electrode at the point of zero charge. The assumption involved in the former method relates to the entropy of transport across a boundary of similar solutions at different temperatures. The corresponding assumption for the latter method is that the temperature dependence of the surface potential of mercury in water is negligible. Consistent values are obtained from both methods: $S^\infty(H^+, aq) = -22.2 \pm 1.4\ J\ K^{-1}\ mol^{-1}$ (Conway 1978), a value that has not been seriously challenged since. Still, a much smaller negative value was suggested more recently by Schmid et al. (2000). It depends on the apparent similarity between the hydration and gas-phase clustering entropies of the hydrogen and the hydroxide ions. However, the adoption of the Schmid et al. value, $S^\infty(H^+, aq) = S^\infty(OH^-, aq) = -5.45\ J\ K^{-1}\ mol^{-1}$ would increase that of fluoride anions to $25.1\ J\ K^{-1}\ mol^{-1}$, much different from the hydroxide value. However, all measures of the hydration of hydroxide and fluoride anions in aqueous solutions lead to commensurate values. On the other hand,on the basis of Conway's choice (Conway 1978), the value of $S^\infty(OH^-, aq) = 11.3\ J\ K^{-1}\ mol^{-1}$, is quite near that of the fluoride anion, $S^\infty(F^-, aq) = 8.4\ J\ K^{-1}\ mol^{-1}$, and is to be preferred. The derived values for other ions are shown in Table 2.2.

Frank and Robinson (1940) suggested that partial molar entropy of the *water* in an electrolyte solution could be used for deciding on the structure-making or -breaking properties of the ions constituting the electrolyte. Gurney (1953) found a linear relationship between the partial molar entropy of aqueous monatomic *ions* and their viscosity B_η coefficients (see Sect. 2.4.3). Later investigators, such as Nightingale (1959), preferred to deal with the standard molar entropy of hydration, because it permitted the extension of such correlations to polyatomic ions due to cancellation of internal mode entropies of these ions and configurational contributions.

2.2.6 The Polarizabilities of Aqueous Ions

The molar refractivity R_D of an electrolyte is additive for the constituent ions if the ions are in an infinitely dilute solution. The expression used for the determination

of R_D uses the refractive index n_D at the sodium D-line (589 nm) for the solution and for pure water, n_{DW}. It is analogous to that for the apparent molar volume, Eq. (2.13), with the ratio $({n_D}^2 - 1)/({n_D}^2 + 2)$ replacing ρ^{-1} and similarly for ${\rho_W}^{-1}$ being replaced by $({n_{DW}}^2 - 1)/({n_{DW}}^2 + 2)$:

$$R_D = \frac{\left(\frac{1000}{\rho}\right)({n_D}^2 - 1)}{({n_D}^2 + 2)} - [(\rho/\rho_W) - c_E M_W/1000\rho_W]\,\frac{({n_{DW}}^2 - 1)}{({n_{DW}}^2 + 2)} \qquad (2.19)$$

Extrapolation to infinite dilution yields ${R_D}^\infty$ that has the dimension of a molar volume. The reported individual ionic values (Marcus 1997) are based on the arbitrary but reasonable value of ${R_D}^\infty(Na^+) = 0.65 \times 10^{-6}\ m^3\ mol^{-1}$, for the infinitely diluted aqueous sodium ions, the same as for isolated ions (See p. 52), because of the inappreciable dependence of the polarizability of the ions on their environment. The values shown in Table 2.1 for isolated ions, R_{DI}, are in fact those obtained for ions in infinitely dilute solutions, independent of the solvent (though mostly for aqueous ions). The polarizabilities of the ions are obtained from the ${R_{DI}}^\infty$ values by means of Eq. (2.2) and correlate to some extent with the sizes of the ions.

2.2.7 Ion Effects on the Surface Tension of Water

The surface tension of water, ${\gamma_W}^*$, is fairly large, 71.96 mN m^{-1} at 298.15 K, due to its hydrogen bonded network. Ions affect the surface tension of their solution, γ, because they are either preferentially sorbed at the surface layer of the water or, more commonly, desorbed from it, compared with their bulk concentrations. This subject is fully discussed in Sect. 4.4.1 and is not further dealt with here.

2.3 Thermodynamics of Ion Hydration

Ions in aqueous solutions are characterized by several thermodynamic quantities in addition to the molar volumes, heat capacities and entropies discussed above. These are the molar changes of enthalpy, entropy, and Gibbs energy on the transfer of an ion from its isolated state in the ideal gas to the aqueous solution. They pertain also to the dissolution of an electrolyte in water, since they can be considered as parts in a thermodynamic cycle in which the electrolyte is transferred to the gas phase, dissociates there into its constituent ions, which are then transferred into the solution. Contrary to thought processes, as described in Sect. 2.2., it is impossible to deal experimentally with individual ions but only with entire electrolytes or with such combinations (sums or differences) of ions that are neutral. The assignment of values to individual ions requires the splitting of the electrolyte values by some extra-thermodynamic assumption that cannot be proved or disproved within the framework of thermodynamics. However, for a theoretical estimation of the individual ionic

values a model is useful. Its success can be demonstrated if the calculated ionic values for the cations and anions add up to the experimental values for the corresponding electrolytes.

2.3.1 Experimental Enthalpies of Hydration of Ions

When an ion is transferred, in a thought process, from its isolated state in the ideal gas phase into water at infinite dilution a large amount of energy is released due to the interaction of the ion with the surrounding water, from which the work needed for creating a cavity for the accommodation of the ion in the water is subtracted. The molar volume of the ion is compressed in this process from RT/P° to the standard partial molar volume in the solution, V_I^∞. The net relevant energetic amount is the change in the enthalpy, $\Delta_{hydr}H_I^\infty$, but, as said, this cannot be determined experimentally for individual ions.

The standard molar enthalpy of hydration of a complete electrolyte, $\Delta_{hydr}H_E^\infty$, is obtained from its experimental heat of solution and theoretical lattice energy. It is also the difference between the critically compiled standard molar enthalpy of formation of the infinitely dilute aqueous electrolyte (Wagman et al. 1982) and the sum of the standard molar enthalpies of formation of the ideal gaseous ions (Table 2.1), weighted according to their stoichiometric coefficients.

$$\Delta_{hydr}H_E^\infty = \Delta_{soln}H_E^\infty - \Delta_{latt}H_E^\infty = \Delta_f H^\infty(\mathrm{E,aq}) - \sum \nu_I \cdot \Delta_f H^\circ(\mathrm{I^\pm, i.g.}) \tag{2.20}$$

In order to split the experimentally available $\Delta_{hydr}H_E^\infty$ values dealing with entire electrolytes into the ionic contribution a value must be estimated for just one ion. Conventional values are obtained on setting $\Delta_{hydr}H^\infty(\mathrm{H^+})^{conv} = 0$ at all temperatures. The 'absolute' value $\Delta_{hydr}H^\infty(\mathrm{H^+,\ aq}) = -1103 \pm 7$ kJ mol^{-1} at 298.15 K results (Marcus 1987) according to the TPTB assumption, equating the standard enthalpies of hydration of the tetraphenyphosphonium and tetraphenylborate ions:

$$\Delta_{hydr}H^\infty(\mathrm{Ph_4P^+}) = \Delta_{hydr}H^\infty(\mathrm{BPh_4^-}) \tag{2.21}$$

Contrary to the case of the heat capacities (Sect. 2.2.4), the values of $\Delta_{hydr}H_I^\infty$ for these bulky ions are quite low compared with those of small ions. Therefore, the uncertainty involved in equating the values for these reference ions is also small. This estimate for the hydrogen ion is compatible with several other reliable values suggested on the basis of other considerations, ranging from -1091 ± 10 to -1104 ± 17 kJ mol^{-1} (Conway 1978). The values for a number of ions are shown in Table 2.3 and are expected to be accurate to within $\pm 7 z_I$ kJ mol^{-1} (Marcus 1997). Since heat is released on the hydration of the ions, the values are all negative as expected and are of similar magnitude for singly charged ions, whether cations or anions. They become less negative with increasing sizes for a given ionic charge, but become considerably more negative, by a factor of the order of z_I^2, for multi-charged ions.

Table 2.3 Thermodynamic quantities of ion hydration at 298.15 K. (Marcus 1997)

Ion	$\Delta_{\text{hydr}} H_{\text{I}}^{\infty}$ kJ mol^{-1}	$\Delta_{\text{hydr}} S_{\text{I}}^{\infty}$ J K^{-1} mol^{-1}	$\Delta_{\text{hydr}} G_{\text{I}}^{\infty}$ kJ mol^{-1}
H^+	−1,103	−131	−1,064
Li^+	−531	−142	−489
Na^+	−416	−111	−383
K^+	−334	−74	−312
Cs^+	−283	−59	−258
NH_4^+	−329	−112	−296
$(CH_3)_4N^+$	−218	−144	
Mg^{2+}	−1,949	−331	−1,850
Ca^2	−1,602	−252	−1,527
Ba^{2+}	−1,332	−205	−1,258
Fe^{2+}	−1,972	−362	−1,864
Fe^{3+}	−4,462	−557	−4,296
La^{3+}	−3,312	−455	−3,155
F^-	−510	−137	−472
Cl^-	−367	−75	−345
Br^-	−336	−59	−318
I^-	−291	−36	−280
SCN^-	−311	−66	−291
NO_3^-	−312	−76	−289
ClO_4^-	−246	−57	−229
$CH_3CO_2^-$	−425	−170	−374
HCO_3^-	−384	−137	−343
$H_2PO_4^-$	−522	−166	−473
CO_3^{2-}	−1,397	−245	−1,324
SO_4^{2-}	−1,138	−249	−1,064
HPO_4^{2-}		−272	
PO_4^{3-}	−2,879	−421	−2,773

At finite concentrations the molar enthalpy of hydration of an electrolyte may be estimated by adding the relative partial molar heat content of the solute, L_{E}, to the sum of the cation and anion values of $\Delta_{\text{hydr}} H_{\text{I}}^{\infty}$. The value of L_{E} is numerically equal to and of opposite sign to the experimentally measurable (Harned and Owen 1958; Robinson and Stokes 1965) enthalpy of dilution of the electrolyte, $\Delta_{\text{dil}} H_{\text{E}}$. At finite concentrations the heat content and the enthalpy of hydration may therefore be smaller or larger than at infinite dilution, depending on the enthalpies involved in the interactions between neighboring ions.

The partial molar heat content of an electrolyte at molality m_{E} is obtainable from the temperature derivatives of the activity coefficient, $\gamma_{\pm}$:

$$L_{\text{E}} = -\nu R T^2 \left(\frac{\partial \ln \gamma_{\pm}}{\partial T} \right)_{P,m} \tag{2.22}$$

where ν is the number of ions in a formula of the solute electrolyte.

2.3.2 Experimental Entropies of Hydration of Ions

The standard molar entropy of hydration of an ion is:

$$\Delta_{\text{hydr}}S_{\text{I}}^{\infty} = S^{\infty}(\text{I}^{\pm}, \text{aq}) - S^{\circ}(\text{I}^{\pm}, \text{g}) \tag{2.23}$$

i. e., the difference between its standard molar ionic entropy in the aqueous solution (Table 2.2) and the standard molar entropy of the isolated ion in the ideal gas phase (Table 2.1). The former of these, the so called 'absolute' standard molar ionic entropies, are based on the chosen value $S^{\infty}(\text{H}^{+}, \text{aq}) = -22.2 \pm 1.4$ J K^{-1} mol^{-1} at 298.15 K, as discussed in Sect. 2.2.5. With the value of $S^{\circ}(\text{H}^{+}, \text{g}) = 108.9$ J K^{-1} mol^{-1} at 298.15 K shown in Table 2.1 this yields $\Delta_{\text{hydr}}S_{\text{I}}^{\infty}(\text{H}^{+}) = -131.1 \pm 1.4$ J K^{-1} mol^{-1} at this temperature.

These standard molar entropies of hydration of ions are related to the effect that ions have on the structure of water (Abraham et al. 1982; Marcus 1994), see Sect. 3.3.3.

2.3.3 Experimental Gibbs Energies of Hydration of Ions

The standard molar Gibbs energy of hydration of an ion, $\Delta_{\text{hydr}}G_{\text{I}}^{\infty}$, can now be obtained from a combination of the standard molar enthalpy and entropy of hydration:

$$\Delta_{\text{hydr}}G_{\text{I}}^{\infty} = \Delta_{\text{hydr}}H_{\text{I}}^{\infty} - T\Delta_{\text{hydr}}S_{\text{I}}^{\infty} \tag{2.24}$$

The value for the hydrogen ion, $\Delta_{\text{hydr}}G^{\infty}(\text{H}^{+}, \text{aq}) = -1,064 \pm 7$ kJ mol^{-1} is derived from the values of $\Delta_{\text{hydr}}H^{\infty}(\text{H}^{+})$ and $\Delta_{\text{hydr}}S^{\infty}(\text{H}^{+})$ given above. The resulting values of $\Delta_{\text{hydr}}G_{\text{I}}^{\infty}$ are shown in Table 2.3 for a number of ions.

The electrostatic component is the major contribution to the standard molar ionic Gibbs energy of hydration as it is for the enthalpy of hydration. Hence, $\Delta_{\text{hydr}}G_{\text{I}}^{\infty}$ can be estimated from the Born expression, resulting from the following thought process. Let an isolated ion in the gaseous phase, $\text{I}^{z\pm}(\text{g})$, be discharged, to produce a neutral particle, for which process the electric self energy $E_{\text{self}}(\text{I}^{z\pm}, \text{g})$ (Eq. (2.1)) must be provided. The neutral particle is then transferred into the bulk of liquid water with no electric energetic component for crossing the gas/liquid boundary being involved. The neutral particle is then charged up to the original value, producing the infinitely dilute aqueous ion, $\text{I}^{z\pm}, \text{aq}^{\infty}$. The energy of interaction with the surrounding water is thereby released, depending on the permittivity of the water $\varepsilon^{*} = 4\pi\varepsilon_0\varepsilon_{\text{W}}{}^{*}$. Here $\varepsilon_{\text{W}}{}^{*}$ is the temperature- and pressure-dependent relative permittivity, and at 298.15 K and ambient pressure $\varepsilon_{\text{W}}{}^{*} = 78.4$. The net effect of this thought process representing the hydration of the ion is the Born expression:

$$\Delta_{\text{hydr}}G_{\text{I}}^{\infty} = \left(\frac{N_{\text{A}}e^2}{4\pi\varepsilon_0}\right) z_{\text{I}}{}^2 r_{\text{I}}{}^{-1} \left(1 - \frac{1}{\varepsilon_{\text{W}}{}^{*}}\right) \tag{2.25}$$

The problem with this mode of calculation is the use of the same value of the radius r_{I} for the ion in the aqueous solution and the isolated state (see p. 50) and the use

of the relative permittivity of pure water for the description of the interaction of the ion with its immediate surroundings, where dielectric saturation, due to the high electric field of the ion, occurs. Various schemes have been proposed to counter these problems, such as adding a quantity Δr to the ionic radius and/or splitting the process into two spatial regions: one adjacent to the ion, where dielectric saturation occurs and $\varepsilon' \approx {n_{\mathrm{DW}}}^2$ (the square of the refractive index) and the other beyond this, where the bulk value $\varepsilon_{\mathrm{W}}{}^*$ prevails, as in the model described in Sect. 2.3.4. The use of such devices permits the estimation of reasonably correct $\Delta_{\mathrm{hydr}}{G_{\mathrm{I}}}^{\infty}$ values (Marcus 1991).

The standard molar Gibbs energy of hydration of the hydrogen ion noted above, $\Delta_{\mathrm{hydr}}G^{\infty}(\mathrm{H}^+, \mathrm{aq}) = -1,064 \pm 7\ \mathrm{kJ\ mol^{-1}}$ is compatible with the estimates $-1,056 \pm 6\ \mathrm{kJ\ mol^{-1}}$ (Marcus 1991) and $-1,066 \pm 17\ \mathrm{kJ\ mol^{-1}}$ (Conway 1978) but not with $-1,113 \pm 8\ \mathrm{kJ\ mol^{-1}}$ obtained from the cluster pair approximation used by Kelly et al. (2006). The assumptions involved in obtaining the latter value lead to a surface potential of water of $\Delta\chi = 0.34 \pm 0.08$ V (Marcus 2008), which, in turn, is not consistent with the recent estimate of $\Delta\chi = 0.1$ V (Parfenyuk 2002) deemed to be the most nearly correct one.

So called 'real' standard molar Gibbs energies of hydration are obtained from the electromotive force of specially constructed cells. These consist of a jet of aqueous solution flowing downward in the middle of a tube, along the inner surface of which another solution, concentric with the jet, flows with a narrow vapor gap between them. The measurable 'real' standard molar Gibbs energy of hydration is:

$$\Delta_{\mathrm{hydr}}{G_{\mathrm{I}}}^{\infty \mathrm{R}} = \Delta_{\mathrm{hydr}}{G_{\mathrm{I}}}^{\infty} + z_{\mathrm{I}} F \Delta\chi \tag{2.26}$$

where the algebraic value of the ionic charge z_{I} is to be used, $F = 96485.3\ \mathrm{C\ mol^{-1}}$ being the Faraday's constant. The uncertainties connected with the value of $\Delta\chi$ make the use of the measurable 'real' standard molar Gibbs energies of hydration unattractive for obtaining individual ionic values for the desired quantity, $\Delta_{\mathrm{hydr}}{G_{\mathrm{I}}}^{\infty}$.

2.3.4 A Common Model for Ion Hydration Thermodynamics

Marcus (1987, 1991) presented a model that is applicable to all the thermodynamic functions of hydration. It follows the thought process of dissolution described at the beginning of Sect. 2.2:

$$\Delta_{\mathrm{hyd}}Y^* = \Delta Y_{\mathrm{Nt}}(r) + \Delta Y_{\mathrm{El1}}(z, r) + \Delta Y_{\mathrm{El2}}(z, r) + \Delta Y_{\mathrm{St}}(z, r) \tag{2.27}$$

Here Y is, for the present purposes, H or S, Y^* is the 'unitary' part, describing the hydration process proper. At 25 °C $\Delta_{\mathrm{hyd}}H^*$ differs by 2.29 kJ mol^{-1} from the standard enthalpy $\Delta_{\mathrm{hyd}}H^{\circ}$ and $\Delta_{\mathrm{hyd}}S^*$ differs by $-18.9\ \mathrm{J\ K^{-1} \cdot mol^{-1}}$ from the standard entropy $\Delta_{\mathrm{hyd}}S^{\circ}$ per mole of ions. These difference quantities pertain to step 6 in the thought process: the relaxation of the fixed points in the ideal gas and solution phases and turning on the full translational degrees of freedom. The numerical values

depend on the standard states of the ions: 0.1 MPa pressure for the ideal gas state and 1 M for the solution.

The term $\Delta Y_{\mathrm{Nt}}(r)$ is the contribution from the hydration of a neutral solute of the same size of the ion (the r dependence), and is related to the cavity formation, step 2 in the thought process. For the enthalpy $\Delta H_{\mathrm{Nt}}(r) = 35 - 267(r_{\mathrm{I}}/\mathrm{nm})$ kJ mol^{-1} and for the entropy $\Delta S_{\mathrm{Nt}}(r) = -22 - 600(r_{\mathrm{I}}/\mathrm{nm})$ J K^{-1} mol^{-1}, obtained by Abraham et al. from gas solubilities (Abraham and Liszi 1980; Abraham et al. 1983).

The interaction of the solute ion with the water in its surrounding (step 4 in the thought process) is described by the electrostatic terms $\Delta Y_{\mathrm{El1}}(z, r) + \Delta Y_{\mathrm{El2}}(z, r)$. The first pertains to the first hydration shell of the ion and the second to water outside this shell. For the Gibbs energy of hydration these two terms read:

$$\Delta G_{\mathrm{El1}} + \Delta G_{\mathrm{El2}} = -\left(\frac{N_{\mathrm{A}} e^2}{8\pi\varepsilon_0}\right) z^2 \left[\left(1 - \frac{1}{\varepsilon'}\right) \frac{\Delta r_{\mathrm{I}}}{r_{\mathrm{I}}(r_{\mathrm{I}} + \Delta r_{\mathrm{I}})} + \frac{\left(1 - \frac{1}{\varepsilon}\right)}{(r_{\mathrm{I}} + \Delta r_{\mathrm{I}})}\right] \quad (2.28)$$

The second term in the square brackets is the Born expression applicable at distances $r_{\mathrm{I}} + \Delta r_{\mathrm{I}}$, i.e., beyond the first hydration shell of thickness Δr. The first term describes the electrostatic interaction inside this shell, characterized by a relative permittivity $\varepsilon' \approx {n_{\mathrm{DW}}}^2$, approximated by the square of the refractive index of water at the sodium D line. With the relevant dε'/dT and dε/dT values for water at 25 °C, the enthalpy of hydration Eq. (2.28) is $\Delta H_{\mathrm{El1}} + \Delta H_{\mathrm{El2}} = -69.5z^2[(0.35(\Delta r_{\mathrm{I}}/r_{\mathrm{I}}) + 1.005)/(r_{\mathrm{I}} + \Delta r_{\mathrm{I}})]$ kJ mol^{-1}. The entropy is then $\Delta S_{\mathrm{El1}} + \Delta S_{\mathrm{El2}} = -4.06z^2[(1.48(\Delta r_{\mathrm{I}}/r_{\mathrm{I}}) + 1.00)/(r_{\mathrm{I}} + \Delta r_{\mathrm{I}})]$ J K^{-1} mol^{-1}. The thickness of the first hydration shell, Δr, depends on the number of water molecules, h_{I}, in it, the hydration number. According to the model (Marcus 1987) $h_{\mathrm{I}} = 0.36|z_{\mathrm{I}}|/(r/\mathrm{nm})$, that is, it is proportional to the charge number of the ion and inversely proportional to its radius. The volume occupied by h_{I} water molecules is $\pi h_{\mathrm{I}} d_{\mathrm{W}}^3/6$, where $d_{\mathrm{W}} = 0.276$ nm is the diameter of a water molecule. Hence the volume of the first hydration shell is given by:

$$\left(\frac{4\pi}{3}\right)[(r_{\mathrm{I}} + \Delta r_{\mathrm{I}})^3 - {r_{\mathrm{I}}}^3] = \frac{\pi h_{\mathrm{I}} {d_{\mathrm{W}}}^3}{6} \quad (2.29)$$

from which the hydration shell thickness Δr_{I} is readily extracted.

The last term in Eq. (2.27), $\Delta Y_{\mathrm{St}}(z, r)$, pertains to the structural changes taking place in the water around the first hydration shell of the ion, step 5 of the thought process of dissolution. The hydrogen bonding in these surroundings is affected by the enhanced hydrogen bond acceptance of the hydration water of anions and the enhanced hydrogen bond donation of the hydration water of cations, and hydrophobic effects of ions such as the tetraalkylammonium ones also operate. The above described model, unfortunately, is not capable of specifying this term directly for the enthalpy of hydration, but it can be calculated from the experimental values. The structural entropy of ion hydration is more fully discussed in Sect. 3.3.3 in relation of the effects of ions on the structure of water.

Table 2.4 shows the various contributions to the enthalpy and entropy of hydration according to this model, Eq. (2.27). The sizes of the hydrated ions, i.e. $r_{\mathrm{I}} + \Delta r_{\mathrm{I}}$ are

Table 2.4 Calculated values of the thickness of the hydration shell, Δr_I, the hydration number h_I, and the contributions to the molar enthalpy and entropy of hydration of representative ions according to the model of Marcus (1987)

Ion	r_I/nm	Δr_I/nm$_I$	h_I	$\Delta_{hyd}H^*$/kJ mol^{-1}				$\Delta_{hyd}S^*$/J K^{-1} mol^{-1}			
				ΔH_{Nt}	$\Delta H_{El1}+\Delta H_{El2}$	ΔH_{St}	$\sum\Delta_{hyd}H$	ΔS_{Nt}	$\Delta S_{El1}+\Delta S_{El2}$	ΔS_{St}	$\sum\Delta_{hyd}S$
Li^+	0.069	0.171	5.2	17	−542	−14	−539	−63	−32	−48	−143
Na^+	0.102	0.116	3.5	8	−447	−3	−442	−83	−26	−11	−120
K^+	0.138	0.075	2.6	−2	−390	14	−378	−105	−22	45	−82
Cs^+	0.170	0.050	2.1	−10	−350	20	−340	−124	−20	68	−76
Me_4N^+	0.280	0.016	1.3	−40	−241	−10	−291	−190	−14	−34	−238
Pr_4N^+	0.379	0.006	0.9	−66	−182	−154	−402	−249	−11	−514	−774
F^-	0.133	0.081	2.7	−1	−396	−11	−408	−102	−23	−37	−162
Cl^-	0.181	0.044	2.0	−13	−337	13	−337	−131	−20	43	−108
I^-	0.220	0.028	1.6	−24	−294	25	−293	−154	−17	84	−87
ClO_4^-	0.240	0.023	1.5	−29	−274	23	−280	−166	−16	76	−106
Mg^{2+}	0.072	0.225	10.0	16	−1,964	−34	−1,982	−65	−130	−113	−308
Ca^{2+}	0.100	0.169	7.2	8	−1,650	−18	−1,660	−82	−101	−60	−243
Ba^{2+}	0.136	0.118	5.3	−1	−1,432	−6	−1,439	−104	−85	−19	−208
CO_3^{2-}	0.178	0.076	4.0	−13	−1,264	−14	−1,291	−129	−74	−48	−251
SO_4^{2-}	0.230	0.045	3.1	−26	−1,085	−2	−1,113	−160	−64	−5	−229
La^{3+}	0.105	0.197	10.3	7	−3,442	−32	−3,467	−85	−398	−108	−591
PO_4^{3-}	0.238	0.057	4.5	−29	−2,309	−35	−2,379	−165	−137	−117	−419
Th^{4+}	0.100	0.236	14.4	8	−6,060	−27	−6,079	−82	−420	−90	−592
$Fe(CN)_6^{4-}$	0.440	0.020	3.3	−83	−2,468	53	−2,498	−286	−146	176	−256

seen to cover a narrow range only, from a minimum of 0.213 nm for K^+ through not much larger values for the alkali metal and halide ions up to 0.385 or 0.460 nm for the bulky ions Pr_4N^+ and $Fe(CN)_6^{4-}$, a factor of ~2, compared to a factor of > 6 for the radii of the bare ions. The hydration numbers h_I derived from this model are similar to values obtained from diffraction or computer simulation studies or the compressibility of the solutions (Marcus 1997).

The molar enthalpy of hydration is seen to be strongly dominated by the combined electrostatic terms for all the ions, and increases (becomes more negative) sharply with the ionic charge, z_I. Except for the tetraalkylammonium ions the neutral and water- structural contributions tend to cancel each other to an appreciable extent. The hydrophobic effect ΔH_{St} is very marked for the tetrapropylammonium cation, and bulky ions have fairly important contributions from the cavity formation term, ΔH_{Nt}. The model does not distinguish between cations and anions, since the charge enters the expressions squared or as the absolute value.

On the contrary, the molar entropy of hydration is *not* dominated by the sum of the electrostatic terms except for small highly charged ions. The neutral and water-structural terms are of opposite sign for the alkali metal and halide ions but of the same, negative, sign for more highly charged ions. These two terms together are responsible to the large molar entropy of hydration of the tetrapropylammonium cation, but highly charged and highly hydrated small cations, such as La^{3+} and Th^{4+} also have large negative entropies of hydration, but for different reasons.

2.4 Ion Transport

Ions in solution move around spontaneously in an isotropic manner due to their thermal energy and they may carry some of their hydration shells with them, depending on how strong the bonding between the ion and the water of hydration is. The speed of their movements is a quantity that can be determined experimentally for individual ions, contrary to the thermodynamic quantities dealt with above. The directional movement of ions depends on the presence of fields, i.e., gradients in the forces that cause the ions to migrate. An external field could be a pressure gradient, causing the flow of the solution as a whole. It could be an electrical field, causing ions of opposite charges to move in opposite directions. A directional concentration gradient at finite concentration causes directional diffusion of ions. The inherent movement of ions in the absence of a field is their self-diffusion and can occur at infinite dilution or at finite ones in a homogeneous solution.

2.4.1 Self-diffusion of Ions

The rate of self-diffusion of ions is commonly obtained from other transport quantities, such as the conductivity. It may, however, be determined directly by labeling the ions isotopically. It is then assumed that the slight mass difference between ions that

Table 2.5 Transport properties of some ions at 298.15 K. (Marcus 1997)

Ion	D_I^∞ $10^{-9}m^2\ s^{-1}$	λ_I^∞ $cm^2\ \Omega^{-1}\ mol^{-1}$	r_{ISt} nm	B_I M^{-1}
H^+	9.311	349.8	0.026	0.068
Li^+	1.029	38.7	0.238	0.146
Na^+	1.334	50.1	0.184	0.085
K^+	1.957	73.5	0.125	−0.009
Cs^+	2.056	77.3	0.119	−0.047
NH_4^+	1.958[a]	73.6	0.125	−0.008
$(CH_3)_4N^+$	1.196	44.9	0.205	0.123
Mg^{2+}	0.706	106.1	0.174	0.385
Ca^2	0.792	119.0	0.155	0.298
Ba^{2+}	0.847	127.3	0.145	0.229
Fe^{2+}	0.719	107	0.172	0.42
Fe^{3+}	0.604	204	0.136	0.69
La^{3+}	0.619	209.1	0.232	0.582
F^-	1.475	55.4	0.167	0.127
Cl^-	2.032	76.4	0.121	−0.005
Br^-	2.08	78.1	0.118	−0.033
I^-	2.045	76.8	0.120	−0.073
SCN^-	1.758	66	0.142	−0.032[b]
NO_3^-	1.902	71.5	0.129	−0.045
ClO_4^-	1.792	67.4	0.137	−0.058
$CH_3CO_2^-$	1.089	40.9	0.225	0.246
HCO_3^-	1.185	44.5	0.207	0.13
$H_2PO_4^-$	0.879	33	0.279	0.34
CO_3^{2-}	0.923	138.6	0.133	0.294
SO_4^{2-}	1.065	160	0.115	0.206
HPO_4^{2-}	0.439	66	0.279	0.382
PO_4^{3-}	0.612	207	0.134	0.59

[a]Calculated from the molar conductivity
[b]From (Marcus 2012)

differ only by their isotopic composition does not affect their rate of diffusion. This should be valid the more so for diffusing hydrated ions for which their mass includes the mass of the water transported with them. A diaphragm cell is employed, with equal concentrations of the electrolyte in the two stirred compartments, in one of which ions of one kind are labeled by a radioactive isotopic tracer. Other methods of measuring diffusion of ions, e.g. by NMR with non-radioactive isotopes, have also been used. The rates of migration of the labeled ion truly measures self-diffusion at the nominal concentrations employed. The value of the limiting diffusion coefficient, D_I^∞, of the order of $10^{-9}\ m^2\ s^{-1}$, is obtained on extrapolation to infinite dilution.

Values of the limiting self-diffusion coefficients of certain common ions at 298.15 K are shown in Table 2.5. It is seen that the more strongly hydrated an ion is, the lower is its rate of self-diffusion, an exception being the hydrogen ion. This ion does not diffuse in water by massive movement of the ion carrying its hydration shell but by the Grotthuss mechanism, according to which the positive charge (i.e., a missing electron) is hopping from one water molecule in the hydrogen bonded network to the next, hence is much faster.

2.4.2 Ionic Conductivities

The most characteristic properties of ions are their abilities to carry an electric current. They do so by moving in the direction of an electrical field gradient imposed externally, cations towards the negatively charged cathode, anions in the opposite direction to the anode. The rate of movement of ions in an electric field is expressed by their mobilities u_I, measuring their speed at unit field, so that the units of u_I are $m\ s^{-1}/V\ m^{-1} = m^2\ s^{-1}\ V^{-1}$.

When an external electric field is imposed on an electrolyte solution by electrodes dipped into the solution, the electric current produced is proportional to the potential difference between the electrodes. The proportionality coefficient is the resistance of the solution, and its reciprocal, the conductivity, is readily measured accurately with an alternating potential at a rate of ~1 kHz in a virtually open circuit (zero current), in order to avoid electrolysis at the electrodes. The conductivity depends on the concentration of the ions, the carriers of the current, and can be determined per unit concentration as the molar conductivity Λ_E. At finite concentrations ion-ion interactions cause the conductivities of electrolytes to decrease, not only if ion pairs are formed (see Sect. 2.6.2) but also due to indirect causes. The molar conductivity Λ_E can be extrapolated to infinite dilution to yield ${\Lambda_E}^\infty$ by an appropriate theoretical expression. The modern theory, e.g., that of Fernandez-Prini (1969), takes into account the electrophoretic and ionic atmosphere relaxation effects. The molar conductivity of a completely dissociated electrolyte is:

$$\Lambda_E = {\Lambda_E}^\infty - S{c_E}^{1/2} + Ec_E \ln c_E + J'(R')c_E - J''(R'')c_E{}^{3/2} \tag{2.30}$$

Here *S*, *E*, *J'*, and *J"* are explicit expressions, containing contributions from relaxation and electrophoretic effects, the latter two depending also on ion-distance parameters *R*.

The limiting molar conductivity ${\Lambda_E}^\infty$ of an electrolyte can be split into the ionic contributions, the ionic limiting molar conductivities ${\lambda_I}^\infty$:

$$\Lambda_E^\infty = \nu_+ {\lambda_+}^\infty + \nu_- {\lambda_-}^\infty \tag{2.31}$$

with the appropriate stoichiometric coefficients. This is done by using experimentally measured (and extrapolated to infinite dilution) transference numbers, ${t_+}^\infty$ and ${t_-}^\infty = 1 - {t_+}^\infty$, such that ${\lambda_+}^\infty = {t_+}^\infty {\Lambda_E}^\infty$, etc. The commonly used units of the molar ionic conductivities are $S\ cm^2\ mol^{-1}$ ($S = \Omega^{-1}$). Values of the limiting ionic molar conductivities ${\lambda_I}^\infty$ for many ions in water at 298.15 K are shown in Table 2.5; they are accurate to $\pm 0.01\ S\ cm^2\ mol^{-1}$.

The mobilities of ions at infinite dilution, ${u_I}^\infty$, are directly proportional to the limiting ionic molar conductivities:

$${u_I}^\infty = \frac{{\lambda_I}^\infty}{|z|\,F} \tag{2.32}$$

as are also the self-diffusion coefficients:

$${D_I}^\infty = \frac{RT{\lambda_I}^\infty}{z^2F^2} \tag{2.33}$$

In fact, the latter have been obtained for most ions from the conductivities rather than from isotope labeling. Ion mobilities (hence molar conductivities and self-diffusion coefficients) increase with increasing temperatures. A five-fold increase in ${\Lambda_E}^\infty$ between 273 and 373 K has been noted. This is mainly because the viscosity of the solvent diminishes in this direction (Table 1.1 and see below). The transference numbers t_+ and t_- are temperature-sensitive too, though only mildly.

The mobility of an ion, hence its electric conductivity, depends on its size and on the viscosity of the solvent, ${\eta_W}^*$ for aqueous solutions. According to Nernst, Stokes, and Einstein, a quantity called the Stokes radius may be assigned to an ion:

$$r_{ISt} = \frac{\left(\frac{F^2}{6\pi N_A}\right)|z_I|}{{\eta_W}^* {\lambda_I}^\infty} \tag{2.34}$$

The parameter 6 in the denominator arises from the assumption of perfect sticking of the hydrated ion in the aqueous environment; otherwise, for perfect slipping, the parameter would be 4. Ionic Stokes radii, shown in Table 2.5, are of the same order of magnitude as the ionic radii r_I measuring the sizes of ions in crystals and solutions, shown in Table 2.2. However, the r_{ISt} are not directly related to the r_I, except for large tetraalkylammonium ions, for which they are substantially the same. In fact, in many cases the Stokes radii are smaller than the crystal ionic radii, although they are supposed to pertain to the hydrated ions and ought to be larger than the latter. Thus, although the r_{ISt} can be calculated formally by Eq. (2.34) they have no physical significance and their use ought to be discouraged (Marcus 2012b). The Walden products of the viscosities of the solvents and the limiting ionic molar conductivities, ${\eta_S}^*{\lambda_I}^\infty$, are approximately constant for the tetraalkylammonium cations (Marcus 2008). Hence, the Stokes radii of these ions are not sensitive to the solvents in which the ions are dissolved.

2.4.3 *Ionic Effects on the Viscosity*

The fluidity of a liquid, its rate of flow under a pressure gradient, is the reciprocal of its viscosity. The dynamic viscosity of water, ${\eta_W}^*$, although rather small compared with that of other liquids, is caused by the extensive network of hydrogen bonds existing in it that must be partly broken for the water to flow (Jenkins and Marcus 1995; Marcus 2009a). Ions affect the dynamic viscosity of the solution, η, some electrolytes enhancing it whereas others diminishing it. The effect is described up to fairly concentrated solutions by the Jones-Dole expression (Jones and Dole 1929):

$$\left(\frac{\eta}{{\eta_W}^*}\right) = 1 + A_\eta {c_E}^{1/2} + B_\eta c_E + \cdots \tag{2.35}$$

The A_η coefficients can be calculated theoretically from the conductivities according to Falkenhagen and Dole (1929):

$$A_\eta = \left(\frac{A_\eta^*}{\eta_W^*}(\varepsilon_W{}^* T)^{1/2}\right) f(\lambda_+{}^\infty, \lambda_-{}^\infty, z_+, z_-) \tag{2.36}$$

where $A_\eta{}^* = 1.113 \times 10^{-5}\ \mathrm{C^2(m\ K\ mol^{-3})^{1/2}}$ and the function $f(\lambda_+{}^\infty, \lambda_-{}^\infty, z_+, z_-)$ is for a symmetrical electrolyte ($z_+ = |z_-| = z$) approximately (Jenkins and Marcus 1995):

$$f = 0.0732 z^2 \frac{(\lambda_+{}^\infty + \lambda_-{}^\infty)}{\lambda_+{}^\infty \lambda_-{}^\infty} \tag{2.37}$$

On the other hand, the B_η coefficients are empirical. The are obtained as the limiting slopes of plots of $[(\eta/\eta_W{}^*) - 1]c_E^{-1/2}$ vs. $c_E^{1/2}$. The B_η coefficients are additive in terms of the constituent ions of the electrolyte and can be split into the ionic values by means of some reasonable assumption. The generally accepted assumption relates to the mobilities of the ions: $B_{\eta+}/B_{\eta-} \approx u_+/u_-$. The equality $B_\eta(\mathrm{K^+}, \mathrm{aq}) = B_\eta(\mathrm{Cl^-}, \mathrm{aq})$, valid over a narrow temperature range, has often been used, but $B_\eta(\mathrm{Rb^+}, \mathrm{aq}) = B_\eta(\mathrm{Br^-}, \mathrm{aq})$ holds over a fairly wide temperature range and is superior. The latter assumption differs by $-0.002 z_I\ \mathrm{M^{-1}}$ from the former (Jenkins and Marcus 1995). Viscosity B_η-coefficients of selected ions at 298.15 K are listed in Table 2.5 (see also Table 3.1 for data on some other ions and on the temperature coefficients dB_η/dT). They are positive for small and multivalent ions but negative for univalent large ions. As the temperature is increased the negative B_η values become less negative and may change sign at a characteristic temperature. This is explained by the diminishing extent of hydrogen bonded structure in the water as the temperature is raised, so that structure-breaking ions have less structure to break.

These algebraic signs have led to the classification of ions into water-structure-makers ($B_{\eta I} > 0$) and water-structure-breakers ($B_{\eta I} < 0$) (Gurney 1953), and such effects are fully discussed in Sect. 3.1.

2.5 Ion-Solvent Interactions

At infinite dilution in water an ion is surrounded by water molecules and its interactions with them are described in Sect. 2.2, 2.3, and 2.4 in terms of measurable quantities. The dependence of these on the concentration is also briefly described there. There are some further aspects of the ion-solvent interactions that merit discussion, as is done here.

The preference of ions to be hydrated rather than be solvated by non-aqueous solvents, as is manifested by the thermodynamic quantities of transfer from water to such solvents has been recently reviewed (Marcus 1996, 2007; Kalidas et al. 2000; Hefter et al. 2002). These quantities depend on the properties of the non-aqueous solvents and are outside the scope of the present book.

The mutual interactions of ions are treated in Sect. 2.6.

2.5.1 Salting-out and -in

Ions are hydrated and they bind water in their solvation shells, causing less 'free' water to be available to accommodate other solutes. Disregarding any direct ion-solute interactions, the presence of ions in a solution then cause an elevation of the activity coefficient y_N of a non-electrolyte solute, marked by subscript N, in a c_E molar solution of an electrolyte by a factor $1/[1-(V_W/1000)h_E c_E]$ in molar units. Here h_E is the sum of the hydration numbers of the ions constituting the electrolyte.

A result of this is a diminution of the solubility of the non-electrolyte solute N in a solvent containing the electrolyte E in order to maintain a constant activity of N at equilibrium with the pure solute. This phenomenon is called 'salting out' and is described up to fairly high c_E by the Setchenov expression:

$$\log\left(\frac{s_N{}^*}{s_N}\right) = k_{NE}c_E \tag{2.38}$$

Here $s_N{}^*$ is the solubility of N in water in the absence of E and s_N is that in its presence. The coefficient k_{NE} is called the Setchenov salting-out constant and depends on the natures of the non-electrolyte and of the electrolyte as well as on the temperature at ambient pressures. The Setchenov expression is taken as the limiting expression, valid for small solubilities, where self-interactions of the non-electrolyte can be disregarded. Because of the proportionality of the left hand side of Eq. (2.38) to c_E, the Setchenov expression pertains also to infinite dilution of the electrolyte and is additive with respect to the contribution of each ion, k_{NI}, to the total $k_{NE} = \Sigma_I\, \nu_I k_{NI}$, the index $_I$ pertaining to the individual ions of the salting agent (cations and anions, including those in mixed electrolytes) and the ν_I being their stoichiometric coefficients. There are some systems where the solubility is enhanced by the presence of the electrolyte so that $k_{NE} < 0$ and salting-in then occurs, but as a rule $k_{NE} > 0$ and the solubility is diminished.

Salting-out and salting-in pertain not only to the solubilities of the non-electrolyte solutes, but also to their volatility, their extractability by solvents immiscible with water, to phase-transfer catalysis, and other phenomena. The salting is not confined to aqueous solutions, where it was primarily studied and applied, but is found in all kinds of solutions of electrolytes, whatever the solvent. Typical solutes to which Eq. (2.38) pertains are non-reactive gases and organic compounds sparingly soluble in water.

The magnitude of k_{NE} for a given salt generally increases with the molar volume of the non-electrolyte, V_N, and for a given solute with the intensity of hydration of the electrolyte. The latter can be described by the electrostriction that the ion causes (Marcus 2011) and this leads to the McDevit and Long (1952) formulation for the Setchenov constant, rewritten as:

$$k_{NE} = \frac{-V_N V_{E\text{-elec}}}{(\ln 10)RT\kappa_{TW}} \tag{2.39}$$

where $V_{E\text{-elec}}$ is the (negative) molar electrostriction by the electrolyte. The direct interactions of the ions of the electrolyte with molecules of the non-electrolyte are

ignored in this approach. Actually, values of k_{NE} predicted by Eq. (2.39) are about three-fold larger than the experimental values (McDevit and Long 1952; Deno and Spink 1963).

Salting-in cannot be described by this formulation and occurs with poorly hydrated ions and/or with non-electrolytes that are more polar than the solvent (have a higher permittivity). An earlier theory, that of Debye and McAulay (1925), related the salting to the electrical work of charging the ions in water compared with that in the presence of the non-electrolyte. This work is proportional to the difference $(1/\varepsilon_r - 1/\varepsilon_{rW})$. When this difference is negative, that is, for highly polar solutes that increase the permittivity, salting-in is predicted. Other early theories of salting-out and -in were reviewed in the book by Marcus and Kertes (1969) and by Conway (1985) among others.

Shoor and Gubbins (1969) applied the scaled particle theory (SPT) to the salting-out and -in, specifically to the solubilities of non-polar gases in concentrated aqueous potassium hydroxide. Masterton and Lee (1970) derived the Setchenov constants from the SPT for more general systems. Their expression is the sum of three individually calculated terms: $k_{NE} = k_{\alpha NE} + k_{\beta NE} + k_{\gamma E}$, where $k_{\alpha NE}$ pertains to the work required for forming a cavity of the size of the solute, $k_{\beta NE}$ pertains to the interactions of the solute in the cavity with its surroundings, and $k_{\gamma E}$ converts from molar to mole-fraction units. The work $k_{\alpha NE}$ for cavity formation in the electrolyte solution does not equal that in the pure solvent, $k_{\alpha N}$, but is somewhat larger due to the increased tightness of the solvent in the presence of the electrolyte. For the calculation of the Setchenov constant for a particular system it is necessary to know the standard partial molar volume of the electrolyte, V_E^{∞}, the diameters σ_I and polarizabilities α_I of its ions, and the diameter σ_N, polarizability α_N, and Lennard-Jones energy parameter (e_N/k_B) of the solute. Fairly complicated expressions result from this theory for the quantities $k_{\alpha NE}$, $k_{\beta NE}$, and $k_{\gamma E}$. The values of $k_{\alpha NE}$ are positive, those of $k_{\beta NE}$ are negative, and salting-in would occur if $k_{\alpha NE} + k_{\beta NE}(+k_{\gamma E}) < 0$. The values of $k_{\gamma E}$ are much smaller than the other terms, and may have either sign, depending on V_E^{∞} but not on N. The SPT, essentially as developed by Masterton and Lee (1970), has since been applied by other authors to describe and predict salting behavior, e.g., (Fromon and Treiner 1979; Treiner 1981). Pawilkowski and Prausnitz (1983) showed that for a given salt k_{NE} follows the linear expression $a_E + b_E(e_N/k_B)$ for non-reactive gases, and listed the ionic a_I and b_I values (based on the convention that their values of OH^- are zero).

Ruckenstein and Shulgin (2002) used the Kirkwood-Buff fluctuation theory to obtain an expression for the salting out (of gases, but applicable to any non-electrolyte solute) in electrolyte solutions. The resulting expression can be re-written as:

$$k_{NE} = -(2.303 \times 2000)^{-1}(G_{WW} - G_{EE} - 2(G_{WN} - G_{WE})) \tag{2.40}$$

where $G_{\alpha\beta} = {}_0\int^{\infty}(g_{\alpha\beta} - 1)4\pi r^2 dr$ is the Kirkwood-Buff integral, $g_{\alpha\beta}$ is the pair correlation function for species α and β (being water W, electrolyte E, or non-electrolyte N) as a function of the distance r between the centers of their molecules. These integrals are related to the partial molar volumes and Eq. (2.40) can be transformed in

dilute solutions to:

$$k_{NE} = -(2.303 \times 2000)^{-1} \frac{-(\partial V_N / \partial c_E)}{V_E^{\infty}} + V_E^{\infty} - V_W^{*} \qquad (2.41)$$

The first term in the square brackets is generally small compared with the other two and may be neglected. Salting-in then occurs in systems where $V_E^{\infty} > V_W^{*}$, i.e., for bulky ions having a molar volume larger than that of pure water, but otherwise salting-out occurs. Mazo (2006) in an equivalent derivation used the measured k_{NE} to evaluate the Kirkwood-Buff integral G_{NE} not otherwise accessible.

On the practical level, another manner of looking at the salting-out, in the case of non-reactive gases, has been proposed by Weisenberger and Schumpe (1996) by means of the empirical expression:

$$k_{GE} = \Sigma_I \nu_I \left[k_I + k_{G25} + h_G \left(\frac{t}{°C} - 25 \right) \right] \qquad (2.42)$$

The index $_I$ pertains to the individual ions of the salting-out agent (cations and anions, including mixed electrolytes), k_I is an ion specific parameter that is relatively independent of the temperature, and k_{G25} and h_G are gas specific parameters. The conventional numerical values for the k_I are shown in Table 2.6, on the basis $k(H^+)^{conv} = 0$. For the cations to a good approximation $k_I/z_I = 0.080 \pm 0.002\ M^{-1}$, with a small increase in the alkaline earth and divalent transition metal series with the ionic radius, but for the alkali metal ions the opposite trend is observed, except for Li^+. The values of $k_I = 0.0648$ for Cr^{3+} and $k_I = 0.1161$ for Fe^{3+} appear to be outliers. For the anions less clear charge and size dependencies are seen, with $k_I/|z_I| = 0.072 \pm 0.007$, and for the halides k_I decreases with increasing size. The gas parameters are normalized to $k(O_2)^{conv} = 0$, with some positive k_I (e.g., 0.0120 for ethene) and some negative (e.g., −0.0159 for ethane) values for different gases, for most of which $h_G < 0$ for $273 \leq t/°C \leq 353$.

The salting out properties of organic solutes, mainly hydrocarbons, were compiled for many salts by Xie et al. (1997). The dependence on the molar volume of the solute, predicted by Eq. (2.39), was confirmed. Conventional salting constants k_I/M^{-1} on the basis $k(H^+)^{conv} = 0$ for benzene are shown in Table 2.6, the value for HCl yielding the Cl^- value, that for NaCl then the Na^+ value, and these served as secondary reference ions. For SCN^- the mean value for LiSCN and CsSCN was used, since otherwise the anion value would be an outlier. There is good qualitative agreement between the gas salting by the ions and the salting of benzene, but in the latter case instances of salting-in ($k_I < 0$) by large ions are noted.

2.5.2 *Preferential Solvation of Ions in Aqueous Mixed Solvents*

Different considerations are applied when the non-electrolyte is a solvent S miscible with water and is present at an appreciable concentration whereas the electrolyte is

Table 2.6 Ionic salting out parameters k_I/M^{-1} of gases according to Eq. (2.42) from (Weisenberger and Schumpe 1996) and of benzene from (Xie et al. 1997)

Cation	k_I(gases)	k_I(benzene)	Anion	k_I(gases)	k_I(benzene)
H^+	0	0	F^-	0.0920	0.115
Li^+	0.0754	0.094	Cl^-	0.0318	0.048
Na^+	0.1143	0.137	Br^-	0.0269	0.018
K^+	0.0922	0.108	I^-	0.0039	−0.042
Rb^+	0.0839	0.092	OH^-	0.0839	
Cs^+	0.0759	0.040	HS^-	0.0851	
NH_4^+	0.0556	0.055	CN^-	0.0679	
Mg^{2+}	0.1694	0.174	SCN^-	0.0627	−0.032
Ca^{2+}	0.1762		NO_2^-	0.0795	
Sr^{2+}	0.1881	0.176	NO_3^-	0.0128	−0.018
Ba^{2+}	0.2168	0.238	ClO_3^-	0.1348	−0.016
Mn^{2+}	0.1463		BrO_3^-	0.1116	
Fe^{2+}	0.1523		IO_3^-	0.0913	
Co^{2+}	0.1680		ClO_4^-	0.0492	−0.041
Ni^{2+}	0.1654		IO_4^-	0.1464	
Cu^{2+}	0.1675		HCO_3^-	0.0967	
Zn^{2+}	0.1537		HSO_3^-	0.0549	
Cd^{2+}	0.1869		$H_2PO_4^-$	0.0906	
Al^{3+}	0.2174		HCO_2^-		0.029
La^{3+}	0.2297		$CH_3CO_2^-$		0.028
Ce^{3+}	0.2406		$C_2H_5CO_2^-$		0.021
Th^{4+}	0.2709		CO_3^{2-}	0.1423	
$(CH_3)_4N^+$		−0.303	SO_3^{2-}	0.1270	
$(C_2H_5)_4N^+$		−0.625	SO_4^{2-}	0.1117	0.274
			HPO_4^{2-}	0.1499	
			$S_2O_3^{2-}$	0.1149	
			PO_4^{3-}	0.2119	
			$Fe(CN)_6^{4-}$	0.3574	

present at a low concentration. The ions are then solvated by both components of the mixed solvent: water (W) and the organic solvent (S). Its near environment generally has a composition differing from that of the bulk mixture due to preferential solvation of the ion by one of the components. If an ion $I^{\pm}$ has a favorable Gibbs energy of transfer from water into the pure organic component of the mixture: $\Delta_t G^{\infty}(I^{\pm}, W \rightarrow S) < 0$, then it will be preferentially surrounded by molecules of S, otherwise it will be preferentially hydrated. This statement must be modified in view of the mutual interactions of the solvent components of the mixture. When the preferential solvation (hydration) in the mixture is practically complete selective solvation (hydration) is said to takes place. It is of interest to enquire what fraction of the solvation shell of the ion is occupied by each solvent component, and there are two approaches that have been used in order to deal with this question (Marcus 2002).

The following model is employed in the quasi-lattice quasi-chemical (QLQC) approach (Marcus 1983a). The ion $I^{\pm}$ and the molecules of the two solvents, W and S, are distributed on sites of a quasi-lattice characterized by a lattice parameter Z that specifies the number of neighbors each particle has, independently of the nature of the

particles. Note the difference from the QLQC treatment of binary solvent mixtures dealt with in Sect. 1.2.4. The total configurational energy of the system is determined by the sum of the pair-wise interaction energies e_{IW}, e_{IS}, e_{WW}, e_{WS}, and e_{SS}, weighted according to the numbers of the corresponding nearest neighbors, N_{IW}, N_{IS}, etc. These pair-wise energies are assumed to be independent from the other neighbors the partners of the pair have. Ideal entropy of mixing of the particles on the quasi-lattice sites is assumed. The quasi-chemical aspect relates to the relative strength of the mutual interactions of the solvent molecules and those with the ion. A set of equations is provided by this approach to determine the local mole fraction of each of the mixed solvent components, made up from $n_W + n_S$ moles of the components around the ion present at infinite dilution. The relative interaction energy of the ion with W and S is obtained from its standard molar Gibbs energy of transfer from W to S:

$$\Delta E_{I,WS} = \frac{\Delta_t G^{\infty}(I^{\pm}, W \rightarrow S)}{Z} \tag{2.43}$$

The mutual interaction of W with S is obtained from the molar excess Gibbs energy at the equimolar composition in the absence of the ions:

$$\exp\left(\frac{\Delta E_{WS}}{RT}\right) = \left[\left\{2\exp\left(\frac{-G^{E}{}_{WS(x=0.5)}}{ZRT}\right)\right\} - 1\right]^2 \tag{2.44}$$

leading to:

$$\frac{N_{WS}}{Z(n_W + n_S)} = \frac{1 - \left\{1 - 4x_W x_S\left(1 - \exp\left(\frac{-\Delta E_{WS}}{RT}\right)\right)\right\}^{1/2}}{2\left(1 - \exp\left(\frac{-\Delta E_{WS}}{RT}\right)\right)} \tag{2.45}$$

The ratio of the like pairs of solvent molecules is:

$$\frac{N_{SS}}{N_{WW}} = x_S - \frac{\frac{N_{WS}}{Z(n_W + n_S)}}{x_W - \frac{N_{WS}}{Z(n_W + n_S)}} \tag{2.46}$$

The local mole fraction of component W is:

$${x_{IW}}^{L} = 1 - {x_{IS}}^{L} = \frac{1}{1 + (N_{SS}/N_{WW})^{1/2}\exp(\Delta E_{I,WS}/2RT)} \tag{2.47}$$

and the hydration number of the ion is then $Z \cdot {x_{IW}}^{L}$. The equilibrium constant for the replacement of S by W is (Marcus 1988a):

$${K_S}^{W} = \frac{{x_{IW}}^{L} x_S}{x_W {x_{IS}}^{L}} \tag{2.48}$$

The standard molar Gibbs energy of transfer of the ion $I^{\pm}$ from water to the mixture, $\Delta_t G^{\infty}(I^{\pm}, W \rightarrow W + S)$ serves to establish the lattice parameter Z within ± 2 units by fitting the data.

The inverse Kirkwood-Buff integral method (IKBI) does not involve a model such as the QLQC method does, hence is rigorous (Ben-Naim 1988). Note, again, the differences with respect to the treatment of binary solvent mixtures in Sect. 1.2.4. It requires the derivatives of the Gibbs energy of transfer:

$$D = \frac{\mathrm{d}\Delta_t G^{\infty}(I^{\pm}, W \rightarrow W + S)}{\mathrm{d}x_S} \tag{2.49}$$

and of the excess Gibbs energy of mixing with respect to the mixed solvent composition:

$$Q = RT + \frac{x_A x_B \mathrm{d}^2 G^E{}_{A,B}}{\mathrm{d}x_B{}^2} \tag{2.50}$$

These functions, however, may often not be known sufficiently accurately for obtaining meaningful derivatives. The Kirkwood-Buff integrals need for their evaluation in addition to these derivatives also the isothermal compressibility of the mixture, κ_T,and the partial molar volumes of the ion, V_I, and the two solvent components in the mixture as a function of the solvent composition. These integrals are then:

$$G_{W,I} = RT\kappa_T - V_I + \frac{x_S V_S D}{Q} \tag{2.51}$$

$$G_{S,I} = RT\kappa_T - V_I + \frac{x_W V_W D}{Q} \tag{2.52}$$

The expressions yielding the local mole fraction of water around the ion $x_{IW}{}^L$ requires furthermore an estimate of the correlation volume, i.e., the volume around the ion in which it affects the composition of the local solvent mixture. This must be calculated iteratively, because the volume occupied by the solvents around the ions depends on the composition when the components differ considerably in their molar volume, as is to be expected when one of them is water.

$$V_{cor} = 2522.5\ [r_I + 0.1363(x_{IW}{}^L V_W + x_{IS}{}^L V_S)^{1/3} - 0.085]^3 \tag{2.53}$$

The preferential hydration parameter is finally obtained as

$$\delta x_{IW} = x_{IW}{}^L - x_W = \frac{x_W x_S (G_{WI} - G_{S,I})}{(x_W G_{W,I} + x_S G_{S,I} + V_{cor})} \tag{2.54}$$

There exists also the problem in obtaining the required information from experimental data, in that the latter pertain to entire electrolytes, and their application to single ions has some bearing on the meaning of the Kirkwood-Buff integrals. Application of the TPTB assumption (see p. 65) to the splitting of the standard molar Gibbs

Table 2.7 Aqueous solvent mixtures in which the preferential solvation of ions was stutied by the QALQC and IKBI methods (Marcus 2002)

Co-solvent S	Ions	QLQC	IKBI
Methanol	Na^+, Cl^-	✓	✓
Ethanol	K^+, Cl^-	✓	✓
Tetrahydrofuran	H^+, $CH_3CO_2^-$	✓	
Dimethylsulfoxide	Li^+, Na^+, Cs^+, Ag^+, Cl^-, Br^-, I^-	✓	✓
Acetonitrile	H^+, Na^+, Ag^+, Cu^+, Cu^{2+}, Cl^-, $CH_3CO_2^-$	✓	✓
Pyridine	Zn^{2+}, F^-, Cl^-, Br^-, I^-, $C_6H_5CO_2^-$	✓	

energy of transfer of an electrolyte into the ionic contributions has been employed to circumvent this theoretical problem (Marcus 2002).

Both methods have been applied to several ions in aqueous solvent mixtures, with fair agreement when they have been applied to a given system (Marcus 2002). Some systems studied are presented in Table 2.7.

2.6 Ion-Ion Interactions

Beyond infinite dilution, at practical concentrations, ions in solution are sufficiently near each other to interact electrostatically: ions of like charge sign repel each other and those of unlike charge sign attract each other. The average distance apart of the ions, Sect. 2.2.1., is constrained by their concentrations:

$$d^{\mathrm{av}} = {N_{\mathrm{A}}}^{-1/3}\Big(\sum \nu_{\mathrm{I}} c_{\mathrm{I}}\Big)^{-1/3} = 1.1844\Big(\sum \nu_{\mathrm{I}} c_{\mathrm{I}}\Big)^{-1/3}\ \mathrm{nm} \qquad (2.11)$$

At 1 molar concentration and above d^{av} is commensurate with the sizes of ions with their hydration shells in solution: $r_{\mathrm{I}} + 2r_{\mathrm{W}} = d_{\mathrm{I\text{-}O}} + r_{\mathrm{W}}$ (Sect. 2.2.2) (Marcus 2009b).

The electrostatic interactions compete with the thermal movement of all the particles in the solution, ions and water molecules, and are screened by the high dielectric permittivity of the water. The overall interactions, involving ion hydration in addition to ion-ion interactions and the hydrogen bonded network of water are quite complicated. Approximations have to be applied in order to handle the resulting behavior of the ions theoretically.

The 'restricted primitive model' described at the beginning of Sect. 2.2. regards the ions as charged conducting spheres dispersed uniformly in a continuum made up of a compressible dielectric. Within this model and in very dilute solutions of electrolytes the well-known Debye-Hückel theory describes the chemical potentials of the electrolyte, μ_{E}, and that of the water, μ_{W}, sufficiently well.

2.6.1 Activity and Osmotic Coefficients

The chemical potential of the electrolyte, μ_{E}, is directly related to its activity and to its mean ionic activity coefficient, $\gamma_{\mathrm{E}\pm}$ (on the molal scale) or $y_{\mathrm{E}\pm}$ (on the molar

scale):

$$\mu_{\mathrm{E}} = \mu_{\mathrm{E(m)}}{}^{\infty} + \nu_{\mathrm{E}} RT \ln(m_{\mathrm{E}} \gamma_{\mathrm{E}\pm}) = \mu_{\mathrm{E(c)}}{}^{\infty} + \nu_{\mathrm{E}} RT \ln(c_{\mathrm{E}} y_{\mathrm{E}\pm}) \tag{2.55}$$

Here ν_{E} is the number of ions per formula of the electrolyte. The chemical potential of the water, μ_{W}, is directly related to its activity a_{W}:

$$\mu_{\mathrm{W}} = \mu_{\mathrm{W}}{}^{*} + RT \ln a_{\mathrm{W}} \tag{2.56}$$

The activity of the water is roughly equal to the ratio of its vapor pressure in the solution to that of the pure water: $p_{\mathrm{W}}/p_{\mathrm{W}}{}^{*}$ (when the vapor pressures are small and the vapors can be considered to approximate ideal gases). The activity of water in the electrolyte solution of molality m_{E} is related to its osmotic coefficient φ_{W} by:

$$\varphi_{\mathrm{W}} = -\left(\frac{1000}{\nu_{\mathrm{E}} m_{\mathrm{E}} M_{\mathrm{W}}}\right) \ln a_{\mathrm{W}} \tag{2.57}$$

where M_{W} is the molar mass of the water (in g mol^{-1}, 1,000/M_1 = 55.51). The osmotic coefficient is also related to the depression of the freezing point and elevation of the boiling point of the water. The vapor pressures and these quantities are used in order to obtain the water activity experimentally, and this, in turn, leads via the Gibbs-Duhem relationship to the activity coefficient of the electrolyte:

$$-55.51 \mathrm{d} \ln a_{\mathrm{W}} = \nu_{\mathrm{E}} m_{\mathrm{E}} \ln(m_{\mathrm{E}} \gamma_{\mathrm{E}\pm}) \tag{2.58}$$

The various methods to obtain the osmotic and activity coefficients experimentally (the latter also from galvanic cells) are described in the classical books by Harned and Owen (1958) and by Robinson and Stokes (1965).

Application of the restricted primitive model leads to the *limiting* Debye-Hückel expression for the mean molal activity coefficient of an electrolyte that pertains to very dilute solutions:

$$\log \gamma_{\mathrm{E}\pm} = -A z_{+} z_{-} I^{1/2} \tag{2.59}$$

where A depends on the temperature ($A = 0.5115$ in water at 298.15 K). The logarithm of $\gamma_{\mathrm{E}\pm}$ is thus proportional to the square root of the ionic strength:

$$I = 0.5 \sum\nolimits_{\mathrm{I}} m_{\mathrm{I}} z_{\mathrm{I}}{}^{2} \tag{2.60}$$

the summation extending over all the ions in the solution that may contain a mixture of electrolytes. This limiting expression is valid only in very dilute solutions, up to, say, $m = 0.01$ m ($\sim$0.01 M) for uni-univalent electrolytes.

Beyond this concentration, and still within the restricted primitive model, the *extended* Debye-Hückel expression should be used:

$$\log \gamma_{\mathrm{E}\pm} = \frac{-A z_{+} z_{-} I^{1/2}}{1 + B a I^{1/2}} \tag{2.61}$$

It is valid, in turn, up to, say, $m = 0.2\,m$ ($\sim$0.15 M). Beyond this concentration, again, or for higher-valent electrolytes, a linear term in the ionic strength, bI, has to be added, up to quite high concentrations. In these extended expressions, B is a temperature-dependent constant 3.291 $\mathrm{nm^{-1}(mol/kg)^{-1/2}}$ in water at 298.15 K and a is the mean distance of closest approach of the ions. This ought to be at least the sum of their radii: $a \geq r_+ + r_-$ or may be equated to their diameters, if considered the same for cations and anions. On the other hand, the coefficient b of the linear term is a completely empirical fitting parameter. For many purposes the universal product $Ba = 1.5\,\mathrm{kg^{1/2}\,mol^{-1/2}}$ at any temperature may be used in Eq. (2.61), leaving the responsibility for fitting the experimental values of $\log \gamma_{\mathrm{E}\pm}$ to the parameter b.

The added empirical quantity bI was replaced by Stokes and Robinson (1948) by an expression in the hydration number of the electrolyte $h_\mathrm{E} = \nu_+ h_+ + \nu_- h_-$, with the stoichiometric coefficients $\nu_+ + \nu_- = \nu_\mathrm{E}$, according to:

$$\log \gamma_{\mathrm{E}\pm} = \frac{-Az_+z_-I^{1/2}}{1 + BaI^{1/2}} - \frac{h_\mathrm{E}}{\nu_\mathrm{E}} \log a_\mathrm{W} - \log[1 + 0.001 M_\mathrm{W}(\nu_\mathrm{E} - h_\mathrm{E})m_\mathrm{E}] \qquad (2.62)$$

Here, again, there are two fitting parameters, the distance of closest approach a and the hydration number h_E. The expression (2.62) accounts for the amount of solvent, water, bound to the ions in the statistical part of the chemical potential.

A key quantity in the Debye-Hückel theory, leading to the values of the constants A and B, is the screening length, κ, the average reciprocal of the radius of the 'ionic atmosphere' surrounding an ion in the solution, made up essentially by ions of the opposite charge. The square of this quantity is proportional to the ionic strength of the solution and also to the reciprocal of the product $\varepsilon_\mathrm{W}{}^* T$:

$$\kappa^2 = \frac{{N_\mathrm{A}}^2 e^2}{1000 \varepsilon_0 \varepsilon_\mathrm{W}{}^* RT} I \qquad (2.63)$$

The numerical value of the screening length is $\kappa = 0.3556(\varepsilon_\mathrm{W}{}^* T/\mathrm{K})^{-1/2}(I/\mathrm{M})^{1/2}$ $\mathrm{nm^{-1}}$ and for water at 298.15 K it is $\kappa = 2.325 \times 10^{-3}(I/\mathrm{M})^{1/2}\ \mathrm{nm^{-1}}$. The dimensionless product κa features in the denominator of the extended Debye-Hückel expression for $\log \gamma_{\mathrm{E}\pm}$ and in the corresponding expression for the osmotic coefficient.

The logarithm of the water activity is given by the Debye-Hückel theory as:

$$\ln a_\mathrm{W} = -\ln \frac{1 + \nu_\mathrm{E} m_\mathrm{E} M_\mathrm{W}}{1000} + \frac{V_\mathrm{W}}{24\pi N_\mathrm{A}} \kappa^3 \sigma(\kappa a) \qquad (2.64)$$

The function $\sigma(\kappa\, a)$ is

$$\begin{aligned} \sigma(\kappa a) &= 3(\kappa a)^{-3}[(1 + \kappa a) - (1 + \kappa a)^{-1} - 2\ln(1 + \kappa a)] \\ &\approx 1 - 1.5(\kappa a) + 1.8(\kappa a)^2 - \ldots \end{aligned} \qquad (2.65)$$

where the approximation is valid for $\kappa a \leq 1$.

An alternative formulation for the activity and osmotic coefficients is that of Pitzer (1979). It includes the Debye-Hückel limiting law, but treats differently its extension

to practical concentrations for fully dissociated electrolytes up to several moles per kg or per dm^3. For 1:1 electrolytes the resulting expressions are:

$$\ln\gamma_{E\pm} = f_\gamma + B_\gamma m_E + C_\gamma {m_E}^2 \tag{2.66}$$

and

$$\varphi_W = 1 + f_\varphi + B_\varphi m_E + C_\varphi {m_E}^2 \tag{2.67}$$

The functions f are the electrostatic Debye-Hückel terms and the B and C coefficients are electrolyte-specific fitting parameters. Factors involving the charge numbers and stoichiometric coefficients have to be included for electrolyte types other than 1:1. Two universal constants, $b = 1.2$ and $\alpha = 2.0$ are employed in the full expressions for B and C as well as the solvent- and temperature-dependent A_φ arising from the Debye-Hückel theory. For details the series of papers by Pitzer and coworkers should be consulted, starting with (Pitzer and Mayoraga 1973).

For very concentrated solutions, in which the activity of the water is $a_W \leq 0.5$, another approach has been found to be useful. This is the BET approach that assumes that the water molecules are adsorbed on the ions of the salt. According to Stokes and Robinson (1948) the expression relating the salt molality m_E and the water activity a_W is:

$$\frac{m_E a_W M_W}{1 - a_W} = \frac{1}{c_{BET} r_{BET}} + \frac{(c_{BET} - 1) a_W}{c_{BET} r_{BET}} \tag{2.68}$$

A plot of the left hand side (with M_W in kg mol^{-1}) against a_W yields the product $c_{BET} r_{BET}$ as the intercept and $(c_{BET} - 1)/(c_{BET} r_{BET})$ as the slope, from which the two parameters r_{BET} and c_{BET} can be extricated. The former, r_{BET}, represents the number of 'binding sites' for water molecules per formula unit of the salt and the latter, $c_{BET} = \exp(\Delta H_{sorb}/RT)$ involves the difference ΔH_{sorb} between the molar enthalpy of 'sorption' of the water on the salt and the molar enthalpy of liquefaction of water vapor (the negative of the enthalpy of vaporization). The parameters r_{BET} and ΔH_{sorb} depend only moderately on the temperature and are shown in Table 2.8 for a number of salts for which a_W data are available at high concentrations (Marcus 2005a). Although the parameter r_{BET} plays the role of a hydration number, it is noted from the entries in Tables 2.3 and 2.8 that these two quantities do not correlate well, since h pertains to dilute solutions and r_{BET} to very concentrated ones, where hydration shells overlap.

2.6.2 Ion Pairing

In electrolyte solutions consisting of relatively poorly hydrated ions the screening of the charges by the aqueous solvent is inadequate to prevent ionic association at sufficiently high concentrations. In most cases the association stops at ion pairing:

Table 2.8 BET parameters for concentrated salt solutions at 25 °C (Marcus 2005a)

Salt	r_{BET}	ΔH_{sorb}/kJ mol^{-1}
LiCl	3.64	7.05
LiBr	3.82	9.32
$LiClO_4$	3.18	7.50
NaOH	3.20	7.34
KOH	3.25	8.26
$MgBr_2$	7.10	9.19
$CaCl_2$	6.73	5.58
$CaBr_2$	7.50	8.57
$Ca(NO_3)_2$	3.86	5.55
$Ca(ClO_4)_2$	6.83	8.68
$ZnCl_2$	3.69	7.73
$ZnBr_2$	4.01	7.40

one cation with one anion. The treatment of ion pairing according to Bjerrum, using the restricted primitive model (see p. 52), can be formulated as follows (Marcus and Hefter 2006). Ions that are nearer each other than the cut-off distance

$$q = \frac{z_+ z_- N_A e^2}{8\pi \varepsilon_0 \varepsilon_W RT} \tag{2.69}$$

are considered to be paired, those at larger distances from each other are free. The cut-off distance q is necessarily larger than the distance of closest approach a. Due to the electrostatic forces, only ions of opposite charge signs are likely to approach each other to a distance $\leq q$.

The equilibrium $C^{z+} + A^{z-} \leftrightarrows C^{z+}A^{z-}$ is governed by the equilibrium constant, K_A. If the fraction α of the c_E molar electrolyte is dissociated and the fraction $1 - \alpha$ is paired, then:

$$K_A = \frac{1-\alpha}{\alpha^2 c_E} \tag{2.70}$$

The association constant arising from Bjerrum's theory is:

$$K_A = \frac{4\pi N_A}{1000} b^3 Q(b) \tag{2.71}$$

where $b = q/a$ is a dimensionless parameter and the function $Q(b) = {}_2\int^b x^{-4}\exp(x)\mathrm{d}x$, with x as an auxiliary variable, is used, the integral being solved numerically. The value of the key variable b at 298.15 K for any solvent (characterized by its ε_r) is given by:

$$\log b = 1.448 + \log|z_+ z_-| - \log\varepsilon_r - \log(a/\mathrm{nm}) \tag{2.72}$$

At other temperatures $\log(298.15\ \mathrm{K}/T)$ should be added to the numerical constant, with the appropriate value of ε_r being used. The distance of closest approach a is taken as the mean diameter of the ions that should not be smaller than the sum of their ionic radii: $a \geq r_+ + r_-$. The values of $\log Q(b)$ have been tabulated (Marcus

1977) and range from −1.358 at $b = 2.1$ (the lowest practical value) through zero for $b = 5.9$ to positive values at large b, for which $Q(b) \approx \exp(b)/b^4$. The association constant K_A is readily calculated from the parameters b and $Q(b)$ and from it and Eq. (2.70) the fraction associated, $1 - \alpha$ is obtained as a function of the concentration c_E.

The dissociated fraction of the electrolyte, α, is commonly obtained from conductivity data, although other techniques have also been widely employed. In the case of the conductivities, expression (2.19) is replaced by:

$$\Lambda_2 = \Lambda_2^{\infty} - S(\alpha c_2)^{1/2} + E(\alpha c_2)\ln(\alpha c_2) + J'(R')(\alpha c_2) - J''(R'')(\alpha c_2)^{3/2} \quad (2.73)$$

recognizing that the actual concentration of the ions is αc_E instead of c_E.

Ion pairing between univalent ions in aqueous solutions with its high relative permittivity is rare, unless they are only poorly hydrated and can approach each other to within $q = 0.357$ nm (at 298.15 K). The ion-ion interactions that may lead to ion pairing of the alkali metal cations and halide anions were discussed by Collins (1997) in terms of their surface charge densities and the competition between ion-water and water-water interactions. He followed Morris (1968, 1969) who studied the solubilities and heats of solution of such salts and Diamond (1963) who pointed out the water-structure-enforced ion pairing that occurs when both cation and anion are large and poorly hydrated. This has recently been demonstrated by Heyda et al. (2010) using molecular dynamics simulations as well as experimental results concerning NH_4^+ ions on the one hand and for the poorly hydrated tetraalkylammonium ions on the other associating with halide anions. Whereas for the small well hydrated NH_4^+ the order of association is $F^- > Cl^- \geq Br^- \geq I^-$, the order is reversed for the poorly hydrated R_4N^+ ions: $F^- < Cl^- < Br^- < I^-$.

For more highly charged ions appreciable ion pairing does occur in aqueous solutions at concentrations of the order of 1 M for 1:2 or 2:1 type salts and even at concentrations of 0.1 M for 2:2 or salts with more highly charged ions. The equilibrium constants for association of the latter (e.g., $MgSO_4$) are of the order of 100–200 M^{-1}.

There is nothing in this formal electrostatic theory, based on the restricted primitive model of the electrolyte solution, to indicate how intimately the cation and anion are bound together in the ion pair. Water molecules penetrate the intervening space in cases where the cut-off distance q is manifold larger than the mean ionic diameters a. It is possible to specify how many solvent molecules separate the cation and the anion if the 'restricted' is removed from the model. A 'contact ion pair' (CIP) is formed if this number is zero, a 'solvent shared ion pair' (SIP) is formed if it is 1, and a 'solvent separated ion pair' (SSIP or S2IP) is formed if it is 2. Several forms of such ion pairs can exist at equilibrium with each other, depending on the electrolyte concentration. Methods for ascertaining the situation with regard to these forms of ion pairs have been reviewed (Marcus and Hefter 2006).

2.7 Charged Macromolecules

Soluble polymers that carry ionically dissociable groups are called polyelectrolytes, ionizing partly or completely to polyions. Synthetic polyelectrolytes generally have a linear polymeric chain, the hydrophobic backbone, to which side groups with hydrophilic ionizable groups are attached. An typical example of a polyelectrolyte is polystyrene sulfonic acid $-[CH_2CH(C_6H_5SO_3^-H^+)]_n-$, a strong, practically completely ionized electrolyte. The covalently attached ions, $-SO_3^-$, are the 'fixed ions' to which correspond mobile 'counter ions' of opposite charge, hydrated hydrogen ions. On the other hand, a weak polyelectrolyte, such as polymethacrylic acid $-[CH_2C(CH_3)(CO_2^-H^+)]_n-$, is only partly ionized, depending on the pH of the solution. Some polyions do not have a hydrophobic backbone but have long chains of hydrophilic moieties that are ionized, an example being polyphosphate detergents.

Such synthetic linear polyelectrolytes have a regularly repeating structure, but less regularity results from graft polymers, where randomly placed segments of different structures are connected in a row and may form polyelectrolytes having a branched backbone. Synthetic polyelectrolytes may also be cross-linked to form water-insoluble ion exchange resins and membranes that can exchange the counter ions with other ones in the imbibed or adjacent solution. Biological examples of polyelectrolytes are proteins and nucleic acids that share many features with synthetic polyelectrolytes, but they too do not have the regular repeating structures of the latter. However, synthetic polypeptides that mimic some of the properties of proteins do have regular repeating structures and therefore are more readily dealt with theoretically.

The special features exhibited by polyelectrolytes, when extensively ionized, compared with individual ions are due to the proximity along the polymeric backbone of charges of the same kind that repulse one another. The fixed ions attached to the polyelectrolyte can never be said to be at infinite dilution, even if the polyelectrolyte itself is at high dilution. Counter-ions with charges opposite to those of the fixed ions tend to associate electrostatically to some extent with the fixed ions or even may do so cooperatively to several fixed ions. The polymer chain itself is affected by the presence of charges of like sign, resulting in its being extended, in contrast with the coiling of uncharged linear polymers due to the entropic effect. If the degree of ionization is low, the polyelectrolyte will take up a more coiled conformation that maximizes the entropy.

Polyelectrolytes are characterized by their degree of polymerization, that is, their average molar mass (MW) and the dispersion of this average, the lengths, l, of the segments along the backbone that carry the charged groups, and the degree of ionization, $0 \leq \alpha \leq 1$. At low degrees of ionization ($\alpha \to 0$) the charged sites are hydrated individually, but as α is increased the hydration water shells start to overlap partly. A highly ionized ($\alpha \to 1$) linear polyion in aqueous solution may then be modeled, e.g., according to Fuoss et al. (1951), as an infinitely long rod with charges at its surface at a uniform charge density, with a cylindrical sheath of water of hydration around the rod. Still, the arrangement of water molecules near

the hydrophobic polymer backbone differs from that near the ionic groups. Counterions, attracted electrostatically to the fixed ions, bring with them their own hydration shells, and if ion pairs are formed, the hydration shells of fixed and counter ions overlap. The complicated picture of the hydration of polyelectrolytes that emerges depends on the flexibility of the polymeric backbone, the segment length l, the extent of ionization, α, the nature of the fixed ions and of the counter ions, and the presence or absence of additional electrolytes in the solution containing or in contact with the polyelectrolyte.

2.7.1 Electrostriction in Polyelectrolyte Solutions

The role played by electrostriction at biological polyelectrolytes, such as proteins and nucleic acids, has already been considered long ago. Cohn and Edsall (1943) concluded that due to the charged groups that ovalbumin contains, electrostriction reduces its specific volume by 2.43 % relative to the value calculated from its amino acid content (McMeekin and Maeshall 1952). The specific volume of rabbit myosin, rabbit tropomyosin, and Pinna tropomyosin (three muscle proteins) in water measured by Kay (1960) indicated a volume contraction by 0.028, 0.040, and 0.030 $cm^3\ g^{-1}$, respectively. These volume reductions were ascribed to electrostriction and were proportional to the number of charged groups (Mauzerall et al. 2002) in the proteins: 270, 376, and 315 per 10^5 g.

Mauzerall et al. employed pulsed photoacoustic measurements on the proteins involved in bacterial photosynthesis and applied the Drude-Nernst equation to estimate the electrostriction:

$$\Delta V = \frac{\kappa_T z_I{}^2 e^2}{8\pi\varepsilon_0 \varepsilon_W{}^2 r_I} \left(\frac{\partial \varepsilon_W}{\partial V}\right)_T \tag{2.74}$$

However, they used the compressibility κ_T of the protein rather than that of water, κ_{TW} that the equation requires. The calculated electrostriction of $-0.030\,nm^3$/pair of ions is compatible with an assumed compressibility of $0.170\,GPa^{-1}$ (that of water is $0.453\,GPa^{-1}$) and a relative permittivity in the immediate vicinity of the protein of 4 ± 1.

Experimental x-ray and neutron scattering data showed that the water in the hydration shell of a protein is 5–25 % denser than bulk water, i.e., it is highly electrostricted. The surface charge density of proteins (Mauzerall et al. 2002) is $\sigma = 0.08 - 0.48\ Cm^{-2}$ and the related field strength is $E = \sigma/\varepsilon_0\varepsilon_W$ (Danielewicz-Ferchmin et al 2003). The chemical potential of the water near the protein surface is reduced by the lower dipole orientation work (reflecting the lower ε_W) compared with pure water. In order for thermodynamic equilibrium to be established water therefore must flow into this high-field region and thereby compressing it. These aspects of protein hydration are further discussed in Chap. 5 (Sect. 5.3.2).

The charges on the walls of ion channels (see Sect. 5.3.3) and the ions passing through them also cause electrostriction of the water, as discussed by several authors

(Sancho et al. 1995; Duca and Jordan 1997; Krasilnikov et al. 2005; Danielewicz-Ferchmin and Ferchmin 2006). The duplex structures formed from single strand nucleic acids is also accompanied by volume changes and by the release of sodium ions to the solution, and appreciable electrostrictive volume diminution was observed for the B conformation of the duplex (Rentzeperis et al. 1993; Marky and Kupke 2000) in the presence of 0.1 M NaCl.

2.7.2 Ion Association of Polyions with Counter-ions

The drastic diminution of the permittivity of the water near the surface of biological polyelectrolytes noted above, is, of course common also to synthetic polyelectrolytes. The consequence of this diminution is association of the fixed ions with mobile counter ions in the solution. Three types of polyelectrolyte solutions are briefly discussed here: a linear strongly acid polyelectyrolyte, such as polystyrene sulfonic acid; a linear weakly acid polyelectyrolyte, such as (partly) neutralized polyacrylic acid; and a polyelectrolyte gel, such as the crosslinked polymethacrylic acid ion exchanger. In the latter, gel-type polyelectrolyte, two distinct phases exist in equilibrium: the gel phase and the outer solution. The treatment of polybases, e.g., (partly) protonated polyvinylpyridine as an example of a linear weak polybase and crosslinked polystryrene-benzyl-trimethyl-ammonium bromide as an example of a strongly basic anion exchanger are completely analogous to the examples discussed. A distinct class of polyelectyrolytes (polyampholytes), however, involves polypeptides and proteins that have both basic and acidic functions, such as arginine and glutamic acid moieties, on the same polymer chain. These are discussed briefly too.

According to the degree of sulfonation of polystyrene, the density of fully ionized groups along the chains can be varied from having only a few sulfonic groups along the polystyrene chain to having a sulfonic group on every phenyl ring. The variability of the relative molar mass M of the polystyrene chains is another parameter to be taken into account, even with fully sulfonated polystyrene. The osmotic pressures Π of aqueous solutions of the acid and sodium salt of sulfonated polystyrene of $M = 2 \times 10^4$ to 1.06×10^6 were related by Wang and Bloomfield (1990) to their mono-molarities c_{mono} (the molar concentration of styrene sulfonated groups) according to:

$$\Pi = RT\varphi c_{\text{mono}} \tag{2.75}$$

where φ is the osmotic coefficient, Eq. (2.57). The latter quantity is related to the charge density parameter ξ by:

$$\varphi = \frac{1}{2\xi} = \frac{1}{4(q/b_l)} \tag{2.76}$$

where q is the Bjerrum cut-off length (for univalent ions), Eq. (2.69), and b_l is the linear charge spacing along the polyelectrolyte chain (it corresponds to the segment

length l for a fully sulfonated polymer). Agreement with measured osmotic pressures of the calculated values was found with the value $\xi = 4.0$, corresponding with $b_l = 0.25$ nm, to $q = 0.5$ nm, and hence to $\varepsilon_W = 56$ in the near surroundings of the polystyrenesulfonate rods.

The expression (2.76) for the osmotic coefficient was previously derived by Lifson and Kachalsky (1954) and by Manning (1969) but shown by Manning to be valid only when $\xi > 1$. For polyelectrolyte solutions free from added salt with $\xi < 1$ the limiting value of the osmotic coefficient is $\varphi = 1 - {}^1/_2\xi$. Only when the fixed charges on the polyelectrolyte are densely spaced, that is, when the average distance b_l between them is smaller than $2q$ so that $\xi > 1$, would the electrical potential cause the (univalent) counter-ions to bind to ("condense on" (Manning 1969)) the fixed ions, thereby reducing the effective value of ξ to the critical value of unity.

The Donnan salt exclusion parameter Γ expresses a property of polyelectrolyte solutions. It describes the bias when a salt is present in the bulk of the solution against the presence of mobile ions in the vicinity of the polyelectrolyte. In the case of the two phase system of a cross-linked ion exchange gel and an outer solution the exclusion is directly measurable experimentally. If the concentration of the salt in the external solution is c_{Eex} and that in the vicinity of the polyelectrolyte is c_{Enear}, then the limiting value of Γ for a concentration c_{poly} of the polyelectrolyte tending to zero is formally defined by:

$$\Gamma = \lim(c_{\mathrm{poly}} \to 0)\frac{c_{\mathrm{Eex}} - c_{\mathrm{Enear}}}{c_{\mathrm{poly}}} \tag{2.77}$$

Manning (1969) showed that when $\xi < 1$ then $\Gamma = \frac{1}{2}(1 - \frac{1}{2}\xi)$ whereas if $\xi > 1$ then $\Gamma = 1/4\xi$. He compared these expectations with experimental data available to him for a variety of polyelectrolytes: sodium polyvinyl sulfate and sodium polyacrylate (of various degrees of neutralization α) and potassium polyphosphate and DNA, having ξ values ranging from 0.29 to 4.20, with good results. Also the expectations for the osmotic coefficients of the sodium polyacrylate and polymethacrylate were well vindicated.

Consider now an aqueous solution of polyacrylic acid that is being titrated with an aqueous sodium hydroxide solution in the absence of added salt in the solution. The degree of ionization of the polyelectrolyte, α, increases as the titration proceeds up to the equivalent point. Polyelectyrolytes tend to be polydisperse, i.e., have polymer chains of different lengths. It is therefore expedient to specify the concentration c_{poly} in terms of the total number of monomeric titratable groups per unit volume, c_{mono}. There are three different types of "sites" on the polymer chain, of which the relative abundance depends on the degree of ionization α and the concentration c_{mono}. The not-yet-neutralized protonated carboxylic groups constitute one type of "sites", the already ionized carboxylate groups constitute another, and carboxylate groups ion-paired with the sodium counter-ions are a third. When the titration is carried out in the presence of excess sodium chloride, the association of the sodium cations with the polyelectrolyte is enhanced due to the common ion effect, but it may be assumed that the chloride anions remain completely mobile. The environment of a given sodium cation at an appreciable value of α, even in very dilute solutions of

the polyelectrolyte, consists of many anions with which it can associate. The ionic atmosphere does not become infinitely dilute with decreasing concentrations of the polyelectrolyte, $c_{\text{poly}} \to 0$.

The course of the titration is described by the following operative expression according to Harris and Rice (1954):

$$p\text{H} + \log a_{\text{Na}+} + \log\left(\frac{1-\alpha}{\alpha}\right) - \log f = pK_{\text{a}} - pK_{\text{ip}} \tag{2.78}$$

Here f is the degree of binding of the sodium counter-ion, K_{a} is the intrinsic dissociation constant for the acid and K_{ip} is that of the ion pair (the reciprocal of its association constant). This treatment assumes random distribution of the three types of sites along the polyelectrolyte chain, but restrictions can be introduced, such as requiring an ionized site to be adjacent to the one where ion pairing takes place. Lifson and Katchalsky (1948) took into account the mutual interaction of neighboring ionized sites, but the final result was the same as Eq. (2.78), i.e., as for the case where no such interaction was considered.

The interactions of the polyion with the counter-ions may not follow the mass action law if the electrostatic potential around the polyelectrolyte is high. This quantity was calculated for polyelectrolyte gels according to several models. The model proposed by Gregor and Gregor (1977) involved a rod of infinite length of radius a, the fixed charges being located along it at random intervals. The solution region in which counter-ions are affected by the potential extended up to a distance R from the center of the rod. Counter-ions of different sizes, a smaller one with radius r_{sm} at a concentration c_{sm} and a larger one with radius r_{la} at a concentration c_{la}, can approach the rod to different distances. A selectivity constant (ratio of binding constants) arises from this difference in the distance of closest approach. The quantity $1/b_l$ is taken to be the average charge per unit length of the rod and leads to the parameter $\lambda = -2q/b_l$, with q given by Eq. (2.69) for univalent ions. Another quantity, α, is implicitly defined by:

$$2(\alpha^2+1)R^{-2}\left(\frac{4\pi\varepsilon_0\varepsilon k_{\text{B}}T}{\text{e}^2}\right) = c_{\text{la}} + c_{\text{sm}} \tag{2.79}$$

Then the selectivity coefficient between the two kinds of ions is:

$$K^{\text{la}}{}_{\text{sm}} = \frac{\lambda\dfrac{(c_{\text{la}}+c_{\text{sm}})}{c_{\text{sm}}}}{1+\alpha\cot(\alpha\ln)\dfrac{(a+r_{\text{la}})}{R} - \tan^{-1}\alpha} - \frac{c_{\text{la}}}{c_{\text{sm}}} \tag{2.80}$$

This expression was tested by Gregor and Greff (1977) with a completely ionized polymethacrylate gel, cross-linked to various extents, 0.2–24 mol %, by ethyleneglycol dimethacrylate (EGDM). They studied the exchange of the small cation K^+ (assigned $r_{\text{sm}} = 0.175\ nm$) and the large cation Me_4N^+ (assigned $r_{\text{la}} = 0.347$ nm) or Et_4N^+(assigned $r_{\text{la}} = 0.400$ nm), on this rod-like cross-linked polyelectrolyte, with a radius $a = 0.21$ nm and a charge density of $1/b_l = 3.23$ unit charges per

nm. The experimental selectivity coefficient, $K^{\mathrm{la}}_{\mathrm{sm\ expt}}$, has a contribution from the osmotic pressure Π and the difference in the partial molar volumes of the ions: $\exp[\Pi(V_{\mathrm{la}} - V_{\mathrm{sm}})/RT]$, a factor multiplying the electrostatic contribution expressed by Eq. (2.80). The values of Π and R are obtained from the swelling of the polyelectrolyte gels in water.

However, the permittivity ε_{W} of the water in the annular region around the polyelectrolyte defined by R, which enters the distance q according to Eq. (2.69), cannot be estimated independently. Considering Eq. (2.80) as valid, Gregor and Greff (1977) derived a value of the permittivity in the vicinity of the polyelectrolyte rod of $\varepsilon_{\mathrm{W}} = 30 \pm 3$ from the K^+/Me_4N^+ exchange for cross-linking with 4–24 mol % EGDM. However, when the data for the K^+/Et_4N^+ exchange were employed instead the even lower value $\varepsilon_{\mathrm{W}} = 15 \pm 5$ was obtained, for no apparent reason.

Lamm and Pack (1997) subsequently tackled the problem of the estimation of the solvent permittivity near the polyelectrolyte. They employed the finite difference Poisson-Boltzmann technique to calculate the permittivity of water at various distances from a charged cylinder. The effects of the surface boundary, the presence of the fixed ions, that of the counter-ions, and eventually of added electrolyte were considered, all leading in some manner to dielectric saturation, due to electrostriction of the water near the charges. They presented results for a cylinder of 1.0 nm radius and a charge density corresponding to B-DNA, showing the surface effect to be minor but both the fixed and the counter-ions causing a large decrease of the permittivity near the charged cylinder. The total relative permittivity ε_{W} rose from ∼5 at the surface of the cylinder to ∼28 at a distance of 0.5 nm, to ∼45 at 1.0 nm, and ∼58 at 2.0 nm, when there was 50 mM added salt present. In the absence of added salt the values at 0.5 nm (∼38) and at 1.0 nm (∼54) were appreciably larger. A low permittivity of the solvent near the polyelectrolyte is obviously conducive to electrostatic binding of counter-ions to fixed ions.

The association of multivalent ions may introduce complications at both low and high charge densities along the polyelectrolyte chain. When the charge density is low a z-valent cation associates with a single (univalent negative) fixed ion. This causes the sign of the charge of the site to reverse from -1 to $(z-1)^+$ and the site then interacts electrostatically with a neighboring (negatively charged) fixed ion. This may lead to precipitation, if the electrostatic repulsion between the negative sites becomes too small to keep the polyelectrolyte extended. However, when the charge density along the chain is high, multivalent counter-ions associate with several adjacent fixed ions and neutralize the charge. The multivalent counter-ions can also act as cross-linking agents between adjacent chains, when the concentration of the polyelectrolyte c_{poly} is large. This may cause precipitation of the thus crosslinked polyelectrolyte. When the added z-valent ion concentration is increased beyond a certain threshold, however, the screening of the electrostatic attractions permits the polyelectrolyte to be soluble again.

Porasso et al. (2001) showed that coordinative bonding between multivalent counter-ions and the fixed charges is possible beside electrostatic association. When a solution containing Cd^{2+} and polyacrylic acid is titrated with KOH, both 'territorial condensation' of the divalent cation and specific binding occur, whereas in

the presence of Ca^{2+} only the former kind does. Similarly, both condensation and specific binding occur on precipitation and re-solubilization of polyelectrolytes in the presence of multivalent ions, as shown by Sabbagh and Delsanti (2000). Barium ions were able to precipitate all kinds of anionic polyelectrolytes, whether carrying carboxylate, sulfonate, or sulfate fixed ions, whereas other divalent metal ions precipitated only the carboxylate-carrying polyelectrolyes.

Winkler et al. (1998) demonstrated by molecular dynamics the collapse of the extended rod-like polyelectrolyte structure to a coil-like conformation when, in the absence of added salt, the interaction energy of the fixed and counter-ions is increased beyond a certain threshold. Multivalent ions provided sufficiently large interaction energies for a given length of polyelectrolyte and distance between the fixed charges. Polyelectrolytes of finite length had to be used for these simulations, contrary to the infinitely long rods in the models considered above. The end-to-end extension or the radius of gyration was the measure for the collapse of the chain.

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