1

Concepts and Ideas: Setting the Stage

This book is about the nature, behaviour and properties of electrolyte solutions. The types of particles which are present in such solutions are discussed, and the experimental evidence is reviewed, from which the structure and nature of both the solute and solvent species is inferred. The development of the theories which describe the nature of electrolyte solutions is also considered.

But first of all it is useful to gather together in one place most of the facts and ideas which are pertinent and relevant to the understanding of electrolyte solutions. It also helps understanding if an explanation of how and why these facts are relevant is given, and this chapter sets out to do this.

Aims

By the end of this chapter you should be able to:

- describe what is meant by an electrolyte solution;
- list simple properties of ions and consider possible modifications to these properties;
- discuss the molecular structure of water and the effect which ions can have on it;
- discuss the difference between polar and non-polar solvents;
- explain what is meant by dipole, induced dipole and alignment of dipoles;
- list possible ion–ion interactions, ion–solvent interactions and solvent–solvent interactions;

An Introduction to Aqueous Electrolyte Solutions. By Margaret Robson Wright
ISBN 978-0-470-84293-5 (cloth) ISBN 978-0-470-84294-2 (paper)

- distinguish between ideal and non-ideal solutions;
- know what is meant by an ion pair, complex, chelate and micelle;
- understand the significance of base-lines for theoretical predictions about the behaviour of solutions containing free ions only, and their use in determining equilibrium constants for processes in solution;
- appreciate the difficulties involved in distinguishing the various types of associated species in solution.

1.1 Electrolyte solutions – what are they?

Electrolyte solutions are solutions which can conduct electricity. Colligative properties such as the lowering of the vapour pressure, depression of the freezing point, elevation of the boiling point and osmotic pressure all depend on the number of individual particles present in solution. They thus give information about the number of particles **actually** present in solution. For some solutes it is found that the number of particles **actually** present in solution is greater than would be expected from the formula of the compound.

In the study of electrolyte solutions, two types of solute can be distinguished:

- (a) Those where the number of particles present is an integral number of times the number of particles expected on the basis of the stoichiometric unit, such as

  $NaCl(aq)$: 1 stoichiometric unit → 2 particles
  $CaCl_2(aq)$: 1 stoichiometric unit → 3 particles

  and **this ratio does not change with change in concentration**.

- (b) Those, such as ethanoic acid $CH_3COOH(aq)$, or $NH_3(aq)$, where the number is greater than that corresponding to the stoichiometric unit, but is much less than the values found in category (a). Here the ratio of the **actual number** of particles to the **stoichiometric number** of stoichiometric units **increases dramatically with decrease in concentration**.

The electrical conductance of aqueous solutions has been studied. Some are virtually non-conducting, some weakly conducting and some are highly conducting. Conduction of a current through a solution implies the existence of charged particles, and so conducting solutions must contain charged particles – ions. The highly conducting solutions correspond to solutions appearing in category (a), while the weakly conducting solutions correspond to category (b).

X-ray diffraction studies show that some solids consist of discrete molecular units, while others are giant lattices held together by strong electrostatic interactions and with no one cation specifically belonging to any particular anion, and vice versa.

The solutes whose structure in the solid is a giant ionic lattice give strongly conducting solutions whose colligative properties place them in category (a). Colours of ionic solutions are also indicative of individual charged particles being present, for instance, copper salts are always blue, dichromate salts are orange.

The conclusion to be drawn from these studies is that in solution the solute can exist as:

- **Molecular units**: non-conducting, **normal** colligative properties, X-ray structures showing discrete molecular units in the solid.
- **Molecular units plus ions**: weakly conducting, colligative properties showing **slightly** more than the expected numbers of particles present, X-ray structure showing discrete molecular units in the solid.
- **Ions**: highly conducting, colligative properties **considerably greater** than expected, X-ray structure showing a giant ionic lattice.

Solutes giving in solution:

• **Molecular units**	are called **non-electrolytes**
• **Molecular units plus ions**	are called **weak electrolytes**
• **Ions only**	are called **strong electrolytes**

For the weak electrolytes the molecules are present in equilibrium with ions derived from the molecules:

$$\text{molecules} \rightleftharpoons n \text{ ions}$$

$$K_{\text{dissoc}} = \left(\frac{[\text{ions}]^n}{[\text{molecules}]}\right)_{\text{equilibrium}} \tag{1.1}$$

The concept and meaning of equilibrium along with the equilibrium constant are discussed in Chapter 2.

For a **weak electrolyte** which is only partially dissociated into ions at moderate concentrations there is a dramatic increase in the fraction of ions present as the concentration decreases. This shows up directly in the dramatic increase in the molar conductivity as the concentration decreases.

A **strong electrolyte** consists of ions with no significant amounts of molecular species present. The molar conductivity should be independent of concentration, but is not. This will be discussed in detail in Chapter 12.

With extensive study it was soon found that anomalies existed, for instance:

- for strong electrolytes, the molar conductivity is not independent of concentration;
- electrolytes which are strong in aqueous solution are shown to behave like typical weak electrolytes in solvents such as dioxan, acetone, or methanol;
- these anomalies are reflected in other studies using strong and weak electrolytes.

This forced chemists into focusing their attention on two main conceptual points:

- What exactly is an electrolyte solution like, and how does it behave at the **molecular** level? In particular, because ions are charged particles, do electrostatic interactions play a part in the **observable** behaviour of electrolyte solutions?
- What exactly is the role of the solvent, and should its **molecular** properties be included as well as its **bulk** properties?

Attempting to answer these two fundamental questions led to considerable advances in the theory of electrolyte solutions, and in experimental methods with which to quantify and test these theories.

1.2 Ions – simple charged particles or not?

Some simple basic properties of ions are regularly used in the discussion of electrolyte solutions and in theories describing the behaviour of electrolyte solutions. These ideas are often physically naïve and must be modified before a physically realistic description of electrolyte solutions can be given.

These properties are summarised below with indications of which are naïve. A very brief indication of which modifications will be needed is given after the summary. Full discussion of these points is dealt with in later chapters.

1.2.1 Simple properties of ions

- Ions have integral positive or negative charges.
- Ions have finite definite sizes – **but** see discussion below of solvation.
- Ions are often considered to be spherically symmetrical – **but** see discussion below of shapes of ions.
- The charge is normally considered to be evenly distributed over the surface of the ion – **but** see discussion below of charge-separated ions.
- Ions are considered to be unpolarisable – **but** see discussion below of polarising power and polarisability.
- Each ion moves as an independent entity – **but** see discussion below of ion pairing and micelle clustering.
- Ions can be ordered in terms of their ease of discharge at an electrode.
- $H_3O^+(aq)$ and $OH^-(aq)$ show special properties.

1.2.2 Modifications needed to these simple ideas: a summary

Sizes

Sizes of ions in solids are found by X-ray crystallography and are termed 'crystallographic radii'. These radii are often used in discussions of properties of electrolyte solutions. But they really should not be used for ions in solution. Many studies indicate that bare ions rarely exist in solution, and their effective size is a combination of the crystallographic radii plus a contribution from solvation effects. Electrochemical experiments can yield solvation numbers, but the main evidence comes from other studies which will be discussed in Chapter 13. Knowledge about solvation is vital to the understanding of the behaviour of electrolyte solutions and has proved to be of crucial importance in determining the behaviour of biological systems. Because of the considerable current interest in this topic a full chapter will be devoted to solvation.

Shapes

Because so much of the theoretical discussions of electrolyte solutions is based on the assumption that ions are spherically symmetrical, there is the tendency to forget that many ions are certainly not symmetrical. A conscious effort should be made to think about the shape of an ion as well as its charge.

Ions such as Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, PO_4^{3-}, are nearly spherically symmetrical, as are many of the complex ions found in inorganic chemistry:

$$Co(NH_3)_6^{2+} \qquad Fe(CN)_6^{4-}$$
$$Ni(CH_2(COO)_2)_2^{2-} \qquad AlCl_6^{3-}$$

but many organic ions are not, e.g.:

$$^+NH_3CH_2CH_2COOCH_2CH_2C_6H_5CHBrCHBrCOO^-$$

while complex ions, like those which are often found in biologically active solutions, generally are non-spherical.

Modern theories of electrolyte solutions using statistical mechanical ideas are now able to take cognisance of the shapes of ions (see Sections 10.17.3 and 10.19).

Distribution of charge on an ion

Even distribution of charge over the surface of an ion is a valid assumption for simple spherical ions such as Ca^{2+}, SO_4^{2-}, $AlCl_6^{3-}$, but is most probably invalid for ions such as

$$(CH_3)_3N^+CH_2CH_2CH_2CH_3 \qquad CH_3CH_2CH_2COO^-$$

Furthermore, many organic ions, often associated with biologically important substances, have a total charge which is a multiple of one, but where this charge is made up of individual charges at different sites in the molecule, as in

$(CH_3)_3N^+CH_2CH_2N^+(CH_3)_3$	$SO_3^-CH_2CH_2CH_2SO_3^-$
$^+NH_3CH_2COO^-$	$^+NH_3(CH_2CONH)_nCH_2COO^-$
$SO_3^-CH_2CH_2COO^-$	proteins
polyphosphates	nucleotides
polysaccharides	

It is quite obvious that even distribution of charge over these ions simply will not occur, but a further important factor must also be considered. Do these substances behave as ions with a given overall net charge, and can they be treated as though they were equivalent to simple ions such as Ca^{2+}, SO_4^{2-}, or as though each individual charge simulated a separate individual ion? Evidence suggests that in certain solvents and above certain concentrations, effects such as these are highly pertinent to the understanding of the behaviour of these electrolytes.

The behaviour of a charge-separated ion is likely to be different from that of simple ions. Ideas and theories developed for the simple cases will have to be modified for these situations.

Unpolarisable ions

It is clearly untrue to consider ions to be unpolarisable, but theoretical treatments generally discuss ions as though they were unpolarisable.

However, even the simple I^- ion is highly polarisable. This is a well accepted fact in other branches of chemistry. Fajans' Rules in inorganic chemistry deal explicitly with this effect in bonding. In summary:

- small highly charged cations have a strong polarising power because of the intense field around them and can thus have a very strong effect in producing induced dipoles or aligning permanent dipoles in other ions;

and

- large anions with the charge dispersed over a large volume can be very easily polarised by highly polarising cations resulting in induced dipoles in the anion, or alignment of permanent dipoles if present.

These effects are present in the simple ions of standard substances such as Cs^+, Ca^{2+}, Cl^-, SO_4^{2-}, NO_3^-, CH_3COO^- and $(CH_3)_4N^+$. They are also going to be of considerable importance in electrolyte solutions where many of the ions are large and complex, for example protein ions, phospholipid ions, nucleic acids, ions of neurotransmitters and so on. Dipoles, induced dipoles and alignment of dipoles are discussed later (see Sections 1.5, 1.7.2 and 1.7.3).

Complete dissociation into ions

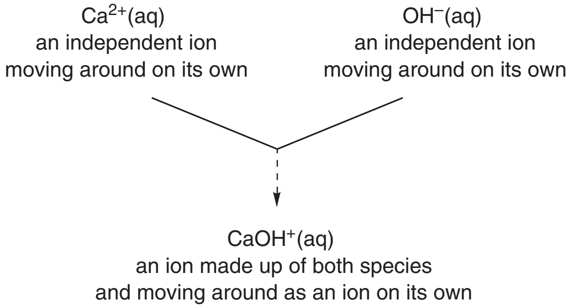
One of the main functions of the solvent is simply to reduce the forces of interaction between ions and thereby reduce the electrostatic potential energy of this interaction. Physically this corresponds to allowing the ions to exist as ions. This is a bulk effect.

Experiments and theoretical considerations, which will be described later, show that:

(a) Increasing the concentration of the solution increases the electrostatic interaction energy between the ions.

(b) Solvents of low polarity result in a greater electrostatic interaction energy between the ions compared with the electrostatic interaction energy between the ions when they are in solvents of high polarity.

There can be situations where the energy of interaction between two ions of opposite charge becomes so high that the ions cease to be independent of each other, and move around as a single unit which survives throughout several collisions before being able to separate. Such a unit is called an **ion pair**. Ion pairs are found in aqueous solutions as well as in low polarity solvents.


$Ca^{2+}(aq)$
an independent ion
moving around on its own

$OH^{-}(aq)$
an independent ion
moving around on its own

$CaOH^{+}(aq)$
an ion made up of both species
and moving around as an ion on its own

This is a very important topic in electrolyte studies and will be referred to often throughout this book.

Ions can also be formed into clusters called **micelles**, and this can become very important in colloidal solutions.

1.3 The solvent: structureless or not?

The solvent is the medium in which the solute exists. It is often called a dielectric. A dielectric can be thought of in terms of an insulator, which is a substance which stops or tends to stop the flow of charge, in other words to stop a current passing through it.

If a substance which acts as an insulator is placed between two charges, it reduces:

a) the field strength;

b) the force acting between the charges;

c) the electrostatic potential energy between the two charges

and the factor by which it reduces these quantities is the relative permittivity, ε_r.

But pay particular attention: what is important is that this definition of the relative permittivity is independent of any assumption that the dielectric is composed of atoms or molecules, and so requires no discussion of the medium at the microscopic level.

In effect, the relative permittivity is just a constant of proportionality characteristic of the medium.

This is precisely what is meant when the medium is described as a structureless dielectric or continuum. In particular, when discussing the role of the solvent in electrolyte solutions it is often described as a continuous medium, or a structureless medium. Most of the theoretical discussions of electrolyte solutions formulate the theoretical equations in terms of factors which involve the macroscopic quantity, ε_r. Use of this bulk quantity in the equations implicitly means a description in terms of the solvent being a structureless dielectric, with no microscopic or molecular structure.

However, the use of a macroscopic quantity in the equations does not preclude a discussion of whether or not it is reasonable, or indeed sensible, to consider the solvent as having a purely bulk macroscopic role to play. Other chemical studies show that the solvent is made up of molecules with a certain microscopic structure, so it is perfectly reasonable to expect that the microscopic structure may be of vital importance when the solvent plays its role as solvent in electrolyte solutions. Indeed, it is precisely by addressing this question that vast progress can be made in the understanding of electrolyte solutions. It is now realised that molecular details of ion–solvent interactions and consequent modifications to ion–ion and solvent–solvent interactions make a significant contribution to the behaviour of electrolyte solutions.

Studies of the microscopic structure of the solvent and its modification by the ions of the electrolyte have resulted in considerable refinements being forced onto the simple model of electrolyte solutions. Unfortunately, it is much easier to alter the model to incorporate new ideas and thought, than it is to incorporate these ideas into the mathematical framework of the theory of electrolyte solutions and its derivation. The implications of many of the topics introduced in this chapter become important in the theoretical treatments of electrolyte solutions (see Chapters 10 and 12, and for solvation, see Chapter 13).

1.4 The medium: its structure and the effect of ions on this structure

The question can be asked:

> **Does the fact that the medium (solvent) reduces the effect of one charge on another charge mean that the charges on the ions must have some effect on the solvent?**

To answer this question the details of the molecular structure of the solvent become important. At this stage some important ideas, developed in more detail in the chapter on solvation, will be introduced briefly.

The solvent is made up of molecules which are in turn made up of nuclei and electrons. In covalently bonded molecules the bonds are formed by sharing of electrons between the two atoms involved in the bond.

- A bond is termed **non-polar** if the electron distribution in the bond is **symmetrical**, i.e. the atoms have an **equal** share of the electrons of the bond.

Examples are: Cl—Cl; H—H; $\text{N}\equiv\text{N}$; C—C

- A bond is termed **polar** if the electron distribution in the bond is **asymmetric**, i.e. the atoms have an **unequal** share of the electrons of the bond.

  Examples are:

$$\text{C}-\text{Cl} \quad \text{written as} \quad \overset{\longrightarrow}{\text{C}-\text{Cl}} \quad \text{or} \quad \text{C}^{\delta+}-\text{Cl}^{\delta-}$$

$$\text{C}-\text{O} \quad \text{written as} \quad \overset{\longrightarrow}{\text{C}-\text{O}} \quad \text{or} \quad \text{C}^{\delta+}-\text{O}^{\delta-}$$

$$\text{H}-\text{F} \quad \text{written as} \quad \overset{\longrightarrow}{\text{H}-\text{F}} \quad \text{or} \quad \text{H}^{\delta+}-\text{F}^{\delta-}$$

$$\text{S}-\text{O} \quad \text{written as} \quad \overset{\longrightarrow}{\text{S}-\text{O}} \quad \text{or} \quad \text{S}^{\delta+}-\text{O}^{\delta-}$$

- When the bond is polar it has a **bond–dipole moment** which, on a qualitative basis, describes the degree to which the electron distribution is asymmetric. The direction in which the electron density is highest is shown by the head of an arrow, e.g. $\text{C}\overset{\rightarrow}{-}\text{Cl}$ and an indication of the relative displacement of +ve and −ve charges is given as $\text{C}^{\delta+} - \text{Cl}^{\delta-}$

- But does this tell us anything about the polarity of the molecule **as a whole?**

Answering this question means looking at the overall effect of the bond dipoles, and this requires knowledge of the symmetry of the arrangement of the atoms in the molecule.

- If **all the bonds** in the molecule are **non-polar**, or **virtually non-polar** (as in C—H), then the molecule as a whole will be **non-polar**;
  for example H_2, N_2, O_2, S_8, alkanes, benzene.

- But if **some of the bonds** are **polar**, then the molecule as such will be:

  - **non-polar** if the arrangement of the atoms is **symmetrical** and the vector bond-dipole moments cancel out, as in CCl_4.

  - **polar** if the arrangement of the atoms is **not symmetrical** enough and the vector bond-dipole moments do not cancel out, as in CH_3Cl, H_2O, CH_3OH.

1.5 How can these ideas help in understanding what might happen when an ion is put into a solvent?

Putting a charge (ion) into a medium (solvent) results in:

↙ partial or complete alignment (dielectric saturation) of the permanent dipoles if the solvent molecule is polar.

↘ displacement of the electrical centres of the molecule if the solvent molecule is non-polar, resulting in an induced dipole.

This effect is greater the nearer the solvent molecule is to the ion, and the higher the concentration of the solution.	This effect is greater the more intense the electric field experienced by the solvent molecule, that is, the more highly polarising the ion is.

- **if the molecule is polar**: alignment of the permanent dipoles is the major effect, but polarisability effects must not be ignored;
- **if the molecule is non-polar**: the only effect comes from induced dipoles and this can be of crucial importance.

Both these effects are of great importance for ion–solvent interactions in solution. In particular, their existence implies that ions **do modify** solvent structure. This, in turn, implies that there must be **consequent modification** of solute–solute interactions in particular, and also of solvent–solvent interactions though these are of relatively less importance.

The relative permittivity, ε_r, of the solvent allows an assessment of the effect of the solvent on the strength of the ion–ion interactions to be made. Coulomb's Law (see Section 10.4.2) states that:

the force of electrostatic interaction between two ions in a solution, $f = \dfrac{z_1 z_2 e^2}{4\pi\varepsilon_0\varepsilon_r r^2}$

so that the larger the relative permittivity, ε_r, the smaller the force of interaction. The value of the relative permittivity, in principle, is measured by observing the effect of an external field on the solution. However, in practice, this experiment is difficult to carry out because it will be complicated by the effect of the external field being predominantly to cause conduction of a current through the solution (see Chapter 12).

Nonetheless it is still possible to talk about the effect of the field **on the solvent**. The ions in a solution can align the permanent dipoles of the solvent and can also induce dipoles in the solvent. The more the dipoles are aligned by the ions the smaller will be the value of the relative permittivity. If the ions have totally aligned all the dipoles in the solvent molecules, there will be none left for the external field to align. The net result is that the only effect that the external field can have will be to induce further dipoles – a much smaller effect. Hence the measured relative permittivity will be low for such a situation.

Furthermore, the possibility of alignment of the dipoles of the solvent molecules by the ions leads to the following conclusion. For the solution, the simplest model to be envisaged is one where three possible situations can be thought of. And for each situation a question can be asked:

- There is a region close to the ion where all the permanent dipoles are **completely aligned** – the region of dielectric saturation.

Question: Can it possibly be valid to use the macroscopic relative permittivity in the theoretical treatments?

- There is a region where **partial alignment** occurs, and the situation changes through the region from **complete alignment** to one where there is **non-alignment**.

Question: What value should be assigned to the relative permittivity here; should it vary throughout the region?

- There is a region where almost **no alignment** occurs and where the solvent behaviour approximates to that of the pure solvent.

Question: Is it legitimate to use the bulk relative permittivity of the pure solvent here? – the answer here is probably 'yes'.

From this very basic and elementary discussion it should be abundantly clear that the solvent plays a crucial role in the behaviour of electrolyte solutions, quite apart from its role as a dielectric reducing the forces of interaction between ions. Such considerations are of vital importance in physical chemistry and have only been tackled rigorously in the past three decades or so. Where complex electrolytes such as are encountered in biological chemistry are concerned, they are of crucial importance and may well dominate the behaviour of such solutions.

1.6 Electrostriction

In the vicinity of each ion, a certain shrinkage of the solvent is likely to occur as a result of the attraction between the ionic charge and the polar molecules. This is called **electrostriction**, and leads to a local increase in the density of the solvent around each ion since more molecules will be packed around the ion than would be present in that volume were the ion not present.

Electrostriction is important in solvation, but has not ever been properly incorporated in any detail into electrolyte theory.

1.7 Ideal and non-ideal solutions – what are they?

Ideality is a concept which can be used for a pure substance **only if** the interactions between the particles are **negligible** as in a gas at low pressures. Since pure liquids and pure solids are condensed phases, there must be **significant** forces of interaction between their fundamental particles. It is, therefore, meaningless to talk about ideality for either the pure liquid or pure solid. But **ideality and non-ideality** are important when talking about **mixtures**.

A two component mixture can alter in composition from the situation where the amount of component A is zero to one where the amount of component B is zero. In between these two limiting situations there are mixtures with varying proportions of the two components. A mixture where the amount of **one** component **tends to zero** corresponds to the **ideal** mixture. Mixtures where there are **finite** amounts of **both** components present correspond to **non-ideal** mixtures.

Electrolyte solutions are mixtures where the components are the solute and the solvent. When the concentration of the solute **tends to zero**, called infinite dilution, the solution is regarded as **ideal**. When there are **finite** concentrations of solute the solution is regarded as **non-ideal**.

In electrolyte solutions there will be interactions between:

- solute–solute particles
- solute–solvent particles
- solvent–solvent particles

In electrolyte solutions the solute is partly or wholly in the form of ions in solution. Because ions are charged particles, there will be electrostatic interactions between the ions, and between the ions and the solvent, over and above the solvent–solvent interactions.

1.7.1 Solute–Solute interactions, i.e. ion–ion interactions

These are basically made up of five contributions:

- **Long-range coulombic interactions**, i.e. those acting over long distances between the ions. These are electrostatic interactions obeying the Coulomb inverse square law (Section 10.4.2).

$$\text{force} \propto r^{-2}$$

- **Ion-induced dipole interactions** if the ions are polarisable, as indeed most ions are (see Section 1.7.3 for a discussion of induced dipoles).
- **Short-range attractions**, i.e. those acting over short distances. These can be coulombic or non-coulombic in nature.
- **Short-range repulsions** which become significant at short distances between the ions. They are always present when two particles approach close to each other.
- **Hard spheres** where the short-range repulsive force becomes infinite when the ions come into contact. It will be seen later (Chapters 10 and 12), that the term ‘into contact’ is not unambiguous and is open to several interpretations.

1.7.2 Solute–solvent interactions, i.e. ion–solvent interactions – collectively known as solvation

These interactions are made up of:

- **Ion–dipole interactions**.
- **Ion-induced dipole interactions**.

(see Section 1.5 and Section 1.7.3 below for a description of these effects.)

These interactions are **attractive** when the interaction is between the end of the dipole which has an opposite charge to that of the ion with which the dipole or induced dipole is interacting.

They are **repulsive** when the ion is in close enough proximity to the end of the dipole which has a charge the same as the ion.

1.7.3 Solvent–solvent interactions

These are as described below, and are the same as are present in a pure liquid, though it must always be remembered that they may well be **altered** or **modified** as a result of the presence of the solute.

The interactions present are:

- **attractions** between solvent molecules;
- **repulsions** between solvent molecules.

The **attractions** for the solvent molecules are mainly associated with permanent or induced dipoles in the molecules.

- **dipole–dipole interactions**: dipoles in one molecule can interact with dipoles in another molecule;
- **dipole-induced dipole interactions**: dipoles in one molecule can interact with another molecule to produce an induced dipole;
- **induced dipole-induced dipole interactions or dispersion forces**: induced dipoles in one molecule can interact with induced dipoles in another molecule;
- **dipole–quadrupole or higher effects**: dipoles in one molecule can interact with quadrupoles in other molecules.

A quadrupole is a distribution of charge more complicated than a dipole. It can be exemplified as:

$$\underline{\delta^- \qquad \delta^+} \qquad \underline{\delta^+ \qquad \delta^-}$$

The molecule CO_2 has a quadrupole of this nature

$$\overset{\delta^-}{\mathrm{O}} = \!= \!= \overset{\delta^+\delta^+}{\mathrm{C}} = \!= \!= \overset{\delta^-}{\mathrm{O}}$$

The **repulsions** for solvent molecules are mainly a consequence of the molecules getting closer together, and finite sizes causing repulsions:

a) quantum mechanical repulsion associated with induced dipole-induced dipole repulsions;

b) permanent dipole–permanent dipole repulsion arising when the geometrical orientation of the molecules in space brings like charge ends of dipoles in each molecule close together.

1.8 The ideal electrolyte solution

In the ideal electrolyte solutions all three interactions are present:

- ion–ion interactions;
- ion–solvent interactions; and
- solvent–solvent interactions,

and the **ideal** electrolyte is defined as the infinitely dilute solution where the **concentration of the solute**, (i.e. the ions) ⟶ **zero**.

Under these conditions:

- solvent–solvent interactions are significant, and are similar to those described in Section 1.7.3 above;
- solute–solvent interactions are present, but are considered to be of less significance than solvent–solvent interactions because the ratio of solute to solvent is very low;
- solute–solute interactions are present, but are considered to be relatively small because of the low concentration of solute.

Repulsions are present, and will be significant for the solvent–solvent interactions, but are considered negligible for solute–solute and solute–solvent interactions because the concentration of solute ⟶ zero.

1.9 The non-ideal electrolyte solution

Physically this corresponds to all concentrations of solute, ions, other than that of infinite dilution where the concentration of the ions ⟶ zero. What contributes to non-ideality can best be explained by considering in turn what happens, as the concentration of solute increases, to the three types of interaction discussed already.

- Non-ideality corresponds to all **ion–ion** interactions **over and above** those considered to be present in the ideal solution. These are any **modified** ion–ion interactions resulting from increase in the solute concentration. This is the major factor giving rise to non-ideality in electrolyte solutions. There will be **three** ion–ion interactions:

- cation and anion interactions,
- cation and cation interactions,
- anion and anion interactions.

There are a large number of modified interactions which can be considered as contributing to the non-ideality of the electrolyte solution. All of them result in increasing non-ideality as the solute concentration increases. They will be discussed in Chapters 10 and 12.

- Non-ideality also corresponds to all **ion–solvent** interactions which are **over and above** those considered to be present in the ideal solution, i.e. any **modified** ion–solvent interactions resulting from the increase in solute concentration. These interactions become more important at **high** concentration, and the contribution of ion–solvent interactions to non-ideality in electrolyte solutions becomes more important at high concentrations. An ion can interact with the solvent and can modify the solvent around it, or two ions could modify the solvent in between them. This would correspond to an ion–solvent interaction different from the ideal case and would lead to non-ideality which would increase as the solute concentration increases. It would also lead to modified solvent–solvent interactions.

- Non-ideality also corresponds to all **solvent–solvent** interactions which are **over and above** those considered to be present in the ideal solution, i.e. any **modified** solvent–solvent interactions resulting from the presence of the solute (cation and anion) at concentrations greater than infinite dilution. However, this is a relatively minor effect and of less importance than contributions to non-ideality which are discussed above. For instance, the cation or anion, or both, could disturb the solvent structure present in the pure solvent, and this in turn would lead to modified solvent–solvent interactions which would then be considered as non-ideal. This modification would become increasingly greater as the solute concentration increases, giving rise to increasing non-ideality.

1.10 Macroscopic manifestation of non-ideality

The **actual** electrostatic potential energy of a real electrolyte solution is a sum of all these possible interactions. Each one makes its own contribution to the total electrostatic potential energy, and each contribution has a different weighting depending on the physical situation being considered. The **ideal** electrostatic potential energy is the sum of all interactions present in the ideal solution where the concentration of solute tends to zero. The difference between the **real actual** potential energy and the **ideal** value represents the **non-ideal** electrostatic potential energy. This can be shown to be equivalent to the **non-ideal** part of the total free energy, G, of the solution, and this non-ideal part of G is often termed the **excess free energy**,

G^E, of the solution (see Chapter 10, Section 10.6.15). This, in turn, can be considered in the simple primitive treatment of electrolyte solutions to manifest itself as an **activity coefficient** $\gamma_\pm$, or in a less primitive version as:

$\gamma_\pm$ **plus a solvation term**.

In modified treatments the excess free energy can be considered to manifest itself as:

$\gamma_\pm$ **plus a solvation term plus an ion pair association term**

and in more advanced treatments the effects of shape, charge distribution, polarising power and polarisability will come in.

The term **mean** activity coefficient is used here, rather than an individual activity coefficient for the cation and the anion, and is defined in Sections 8.22 and 8.23 and Worked Problems 8.13 and 8.14 and below.

The activity coefficient is defined in terms of the activity and the concentration (see Section 8.21.1).

$$a = \gamma c \tag{1.2}$$

Both activity and concentration are experimental quantities. It is possible to **talk** about the activity and the activity coefficient of each type of ion making up the electrolyte, but the activity and the activity coefficient of the **individual** ions **cannot** be measured experimentally. Activity is a property of the electrolyte solution as a whole. Hence the use of **mean** activities and **mean** activity coefficients. The term mean is **not** used in its common sense of an average quantity, but is used in a rather different sense which reflects the number of ions which result from each given formula:

$$\text{NaCl} \longrightarrow 2\,\text{ions}$$
$$\text{CaCl}_2 \longrightarrow 3\,\text{ions}$$

- for symmetrical electrolytes: $\text{AB(s)} \rightarrow \text{A}^{x+}\text{(aq)} + \text{B}^{x-}\text{(aq)}$

$$\gamma_\pm = \{\gamma_{\text{A}^{x+}}\gamma_{B^{x-}}\}^{½} \tag{1.3}$$

e.g. for NaCl:

$$\gamma_\pm^2(\text{NaCl}) = \gamma_{\text{Na}^+}\gamma_{\text{Cl}^-} \tag{1.4}$$
$$\gamma_\pm(\text{NaCl}) = \sqrt[2]{\gamma_{\text{Na}^+}\gamma_{\text{Cl}^-}} \tag{1.5}$$

- for unsymmetrical electrolytes: $\text{A}_x\text{B}_y\text{(s)} \rightarrow x\text{A}^{y+}\text{(aq)} + y\text{B}^{x-}\text{(aq)}$

$$\gamma_\pm = \{(\gamma_{\text{A}^{y+}})^x(\gamma_{\text{B}^{x-}})^y\}^{1/(x+y)} \tag{1.6}$$

and for CaCl_2:

$$\gamma_\pm^3(\text{CaCl}_2) = \gamma_{\text{Ca}^{2+}}\gamma_{\text{Cl}^-}^2 \tag{1.7}$$
$$\gamma_\pm(\text{CaCl}_2) = \sqrt[3]{\gamma_{\text{Ca}^{2+}}\gamma_{\text{Cl}^-}^2} \tag{1.8}$$

This will become much clearer once the thermodynamic description of activity, activity coefficient and mean activity coefficient has been developed (see Sections 8.21 to 8.23).

1.11 Species present in solution

In a solution the solvent is the most abundant species. The solute can exist in various possible forms, but only the following will be discussed.

- Free ions
- Undissociated molecules in equilibrium with free ions
- Ion pairs in equilibrium with free ions and other complexes and chelates
- Complexes and chelates in equilibrium with free ions and other complexes and chelates
- Micelle clusters in equilibrium with free ions

The last four situations are equilibria and an equilibrium constant describes each equilibrium (see Chapter 2). Describing the equilibrium means postulating which species are involved in the equilibrium, which, in turn, requires that:

- it is possible actually to observe the species present by chemical and physical means; or
- chemical judgement suggests that the species do actually exist.

1.12 Formation of ion pairs from free ions

An ion pair is a physical entity with no specific chemical interactions between the ions. The ions of the ion pair move together as a single unit and are held together by electrostatic forces of the coulomb type acting over the short distances that the ions are apart in the ion pair. These coulombic forces impose a certain degree of cohesion on the unit and this is sufficiently great to overcome the tendency for normal thermal motion to cause the ions to move around as separate particles each with its own translational degrees of freedom.

Because the forces holding the ions together are of this physical nature, they depend on three factors:

- the charges on the ions;
- the sizes of the ions;
- the relative permittivity of the solvent in the vicinity of the ion.

It is very important to realise that these forces are therefore **independent** of the **chemical nature** of the ions. On this basis, it would be expected that electrolytes which have ions of the same charge and are of similar size would have equilibrium constants of similar magnitude **if** the associated species is an ion pair. This is found for some 2:2 sulphates, and for some cations of similar size which associate with Cl^-(aq) or I^-(aq).

1.12.1 Charge distribution on the free ion and the ion pair

- The **charge** on a **simple** ion is usually unambiguous, e.g. Mg^{2+}(aq) or NO_3^-(aq), and the charge distribution for such ions is probably approximately spherically symmetrical. But the charge and the charge distribution for some ions may not be so clearly defined, for instance:

$$CH_3CH_2CH_2CH_2NH_3^+(aq)$$
$$(CH_3)_3N^+CH_2CH_2CH_2COO^-(aq)$$

- The **charge** on an **ion pair** is the algebraic sum of the charges on the individual ions:
  - a + 2 cation with a –2 anion gives an ion pair with an **overall** charge of zero, while
  - a + 3 cation with a –1 anion gives an ion pair with an **overall** charge of +2.

However, it is imperative to think more deeply than this.

An ion pair of **zero overall** charge must **not** be treated as though it were a **neutral molecule**. At best it can be regarded as a dipolar molecule, but it is probably more like a charge-separated ion.

- a dipolar ion pair

$$Mg^{2+}(aq) + SO_4^{2-}(aq) \rightleftharpoons (\overrightarrow{MgSO_4})(aq)$$

- a charge-separated ion pair

$$Mg^{2+}(aq) + SO_4^{2-}(aq) \rightleftharpoons (Mg^{2+}SO_4^{2-})(aq)$$

There are important implications arising from this.

If the ion pair is uncharged:

- Interionic interactions between the ion pair and free ions and other ion pairs will be set up and contribute to the non-ideality of the solution.
- The ion pair should be given a mean activity coefficient different from unity. This is rarely done, but see Section 12.17.
- The ion pair will probably be able to conduct a current, though its contribution will be small compared with that from the free ion. It is generally assumed to make a zero contribution, but see Section 12.17.

If the ion pair has an overall charge:

- It should not be treated as though it were a single charge with a spherically symmetrical distribution of charge.
- It is probably more like a dipolar charged ion, e.g. $CaOH^+$(aq) or a charge-separated ion pair $(Ca^{2+}OH^-)$(aq).

- For an overall charged ion pair, a mean ionic activity coefficient must always be assigned to it, generally calculated from the Debye-Hückel theory on the basis of the overall charge.

- It will also have a non-zero molar conductivity, though in practice the magnitude is very difficult to assess.

1.12.2 Size of an ion and an ion pair in solution

Most size correlations for free ions have used crystallographic radii which represent the bare ion. But there is no doubt that most ions are solvated in solution, though it is difficult to assess precisely the extent of solvation, and hence the size of the solvated ion.

Likewise, the ion pair will be solvated, and some estimate of its size is required. Furthermore, the change in solvation pattern on forming the ion pair is of crucial importance.

Three limiting situations can be envisaged, but other intermediate situations are possible:

- An ion pair is formed with no disruption of the individual solvation sheaths of the individual ions, so that in the ion pair these solvation sheaths of the individual ions are in contact and solvent is present between the ions (see Figure 1.1(a)).

- An ion pair is formed with total disruption of the individual solvation sheaths of the individual ions so that in the ion pair the bare ions are in contact and there is no solvent between the ions (see Figure 1.1(b)).

- An ion pair is formed with the partial disruption of the individual solvation sheaths of the individual ions so that in the ion pairs some solvent has been squeezed out, but there is still some solvent present between the ions (see Figure 1.1(c)).

The ion pairs which can be found are thus not necessarily identical, and there is the possibility that different experimental methods may pick out and detect only one kind of ion pair, for instance, detect contact ion pairs but not solvent separated ion pairs.

A further formal definition commonly used in inorganic chemistry can be proposed:

- an **outer-sphere** ion pair is one where one, or at most two, solvent molecules lie between the ions.

- an **inner-sphere** ion pair is one where the bare ions are in contact – all solvent sheaths have been eliminated from between the ions.

However, both inner and outer-sphere ion pairs are still solvated as the **composite** unit, as are the ion pairs described as contact or solvent separated.

Although the **definitions** can be quite unambiguous, **experimental** classification into contact or solvent separated, or inner and outer sphere ion pairs most certainly is not unambiguous, and may even, at best, be only a guess. This is exactly the same problem as is encountered when discussing the formal and experimental distinctions between complexes and ion pairs.

Attempts to distinguish experimentally between the formation of:

a) ion pairs from free ions, and

b) complexes and chelates from free ions

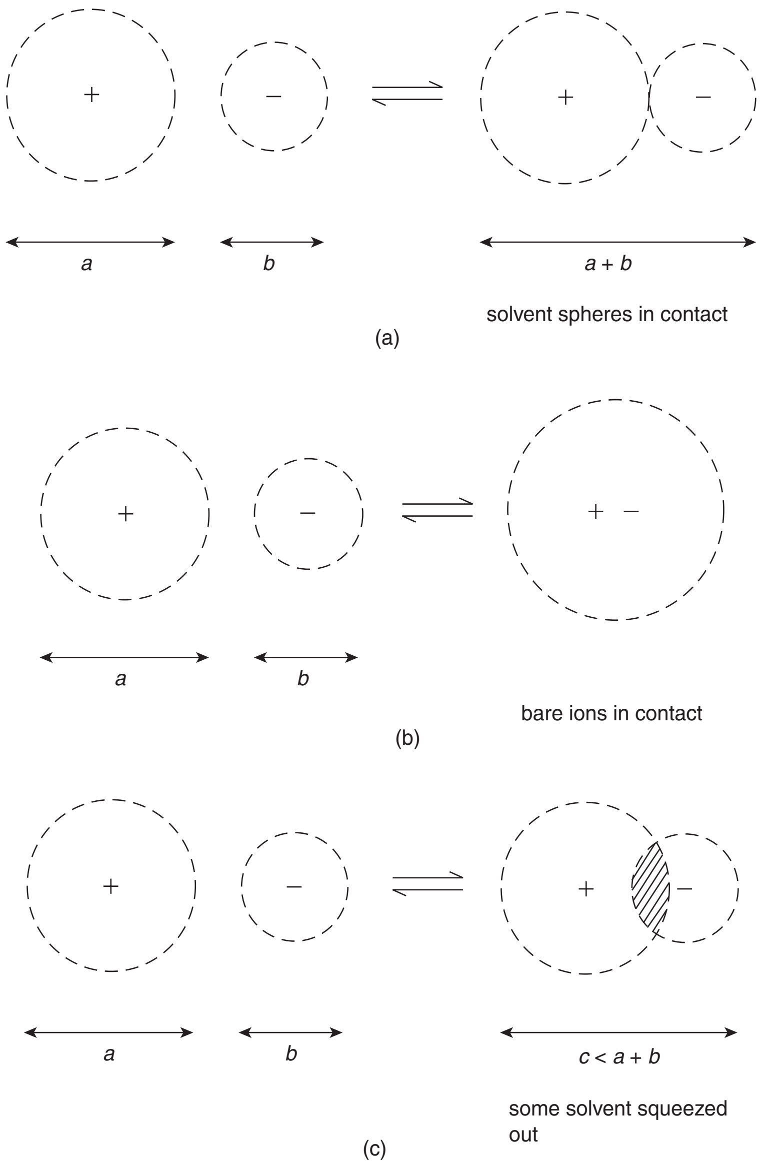


Figure 1.1 (**a**) Solvent sheaths of individual ions in contact; (**b**) bare ions in contact; (**c**) partial disruption of the solvation sheaths of ions showing some solvent being squeezed out.

often end up in deep water, and considerable scepticism must be cast on the interpretation of many experiments which purport to make a clean-cut distinction. Also, different experimental methods may pick up behaviour typical of different types of associated species, so that a comparison of results from different methods may add to the confusion. It is easy to give definitions, but more difficult to decide what sort of species is present.

1.13 Complexes from free ions

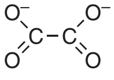
Where a complex is formed there is an intimate chemical interaction between the ions. Some electronic rearrangement is occurring resulting in covalent interactions, in contrast to the physical coulombic electrostatic interactions involved in the formation of an ion pair.

If complexes and chelates involve intimate chemical interactions, the extent of association should reflect the chemical nature of the ions involved. Equilibrium constants should be different, and possibly even very grossly different, for equilibria which superficially seem very similar and alike, for instance, association of one species with ions of similar size and charge. The situation is reminiscent of that found for the dissociation constants of weak acids and bases where the magnitude of the equilibrium constants depends on the chemical nature of the species involved. It is in stark contrast to that expected for the formation of ion pairs, where the magnitude of the association constant is expected to be independent of the chemical nature of the ions involved.

The metal ions:

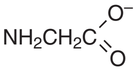
$$\mathrm{Cu}^{2+}(\mathrm{aq}),\quad \mathrm{Ni}^{2+}(\mathrm{aq}),\quad \mathrm{Co}^{2+}(\mathrm{aq}),\quad \mathrm{Zn}^{2+}(\mathrm{aq}),\quad \mathrm{Mn}^{2+}(\mathrm{aq})$$

have crystallographic radii which are very similar, and they all have the same charge, +2. When they interact with oxalate



oxalate

and with glycinate



glycinate

a wide variation in the association constants is found. The glycinates, for instance, have values ranging from 2.75×10^3 to 4.2×10^8 mol^{-1} dm^3. Complexes are assumed to be formed.

On the other hand, it is believed that the interaction of the same metal ions with $\mathrm{SO}_4^{2-}(\mathrm{aq})$ results in an ion pair. Here the association constants are very similar, ranging from 1.9×10^2 to 2.9×10^2 mol^{-1} dm^3.

1.14 Complexes from ions and uncharged ligands

If an associated species is formed between an ion and an **uncharged** ligand, it is usually assumed that a complex is formed and that electronic rearrangements of a chemical nature have occurred.

When aqueous NH_3 is added to an aqueous solution containing Cu^{2+} ions an intense blue coloration indicative of electronic rearrangement occurs, and the main species formed is the complex:

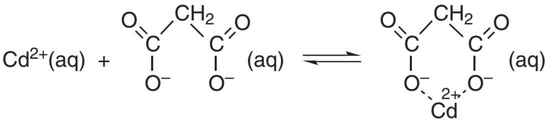
$$\mathrm{Cu}^{2+}(\mathrm{aq}) + 4\mathrm{NH}_3(\mathrm{aq}) \rightleftharpoons \mathrm{Cu(NH_3)}_4^{2+}(\mathrm{aq})$$

Formation of an intimate chemical species implies a fairly drastic alteration in the solvation sphere around the $Cu^{2+}(aq)$, with the NH_3 ligands displacing the solvent molecules from around the ion.

1.15 Chelates from free ions

If the ligand ion is a simple ion, such as $I^-(aq)$ or $OH^-(aq)$, then there is only one possible point of attachment irrespective of whether an ion pair or a complex is formed.

If a ligand has two charges located in different parts of the ion, then there are two possible points of attachment of the cation, and if the interactions are covalent the associated species is called a **chelate**:



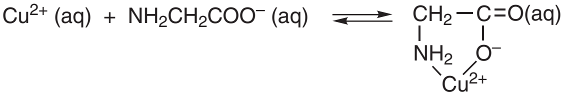
Ligands can be ions as in the example above, but they can also be ions having neutral points of attachment within the molecule, for instance amino acid anions such as glycinates. Does the metal ion then simply ion pair with the carboxylate part, or does the amino part also become involved to form a chelate?, i.e. is the product:

- an ion pair

$$Cu^{2+}(aq) + NH_2CH_2COO^-(aq) \rightleftharpoons NH_2CH_2COO^-Cu^{2+}(aq)$$

or

- a chelate?



Evidence, mainly spectroscopic, suggests that the associated species is a chelate in this case.

Ligands can also be neutral, and act by virtue of their lone pairs, e.g. the standard chelating agent $NH_2CH_2CH_2NH_2$.

1.16 Micelle formation from free ions

Here clustering of ions of like charge occurs to give a cluster of colloidal size. Unambiguous detection of micelle formation is fairly easy experimentally because:

- Formation gives clusters of such a size as to be detected by standard techniques for colloidal solutions such as Tyndall's beam effect where scattering of light by the solution occurs.

- Abrupt removal of such large numbers of ions from solution gives such a dramatic change in the properties of the solution that the effect is easily detected.

Electrolytes showing clustering properties are typified by paraffin chain salts where there is a long paraffin-like chain with a cationic group at the end, as in a quaternary ammonium group:

$$CH_3CH_2CH_2CH_2CH_2CH_2N^+(CH_3)_3$$

or a paraffin-like chain with an anionic group at the end like the carboxylates in soaps, and sulphonates in detergents:

$$CH_3CH_2CH_2CH_2CH_2CH_2COO^-$$

$$CH_3CH_2CH_2CH_2C_6H_4SO_3^{2-}$$

These electrolytes behave like a non-associated electrolyte up to a certain concentration, and then alter abruptly, with the properties changing dramatically. This is attributed to the rapid onset of micelle formation at a certain critical concentration. In the micelle, the paraffin chains face inwards with the charged groups lying on the outer surface where their charge is partially neutralised by small simple ions of opposite charge, ‘counter ions’, fitting into the spaces of the cluster. Overall this has an effect on the properties of the solution similar to that expected if large numbers of ions are removed from solution.

Added salts can encourage the aggregation of ions to micelles, ‘salting out’. This is of considerable importance in biological electrolytes, such as bile salts and phospholipids.

Micelles and polyelectrolytes must always be clearly distinguished. Many biological electrolytes are long chain species, for instance, proteins, where the **individual** molecule or electrolyte is similar in size to the micelle. Many such polyelectrolytes have positive and negative groups occurring alternately or irregularly along the chain. The biggest difference between micelles and biological polyelectrolytes is in the relative mobility of the polymer segments of the polyelectrolyte which are often coiled but can become uncoiled on addition of electrolytes which bind to the polyelectrolyte. In contrast, the micelle can break up into its individual ions, that is, it can come to pieces, whereas the polymer does not. The electrostatic and configurational energy changes are not well understood and represent a challenge to the biologist and chemist alike. Solvation effects are also of major consideration, and have been shown to be of crucial importance.

1.17 Measuring the equilibrium constant: general considerations

This is generally given by comparing the behaviour expected for a given situation with what is actually observed.

The expected or predicted behaviour of the solution is worked out on the basis of a postulate of the solution being made up of free ions only,

and this, in turn,

requires that there is a theoretical base-line which describes the behaviour expected for a solution made up totally of ions,

since

without this theoretical base-line of predicted behaviour it is impossible to start to

infer from the observed experimental behaviour anything about possible species actually present if any of the processes discussed in Sections 1.13 to 1.17 occur,

because

it is precisely the deviations from this base-line which are used to infer the existence of particles other than free ions.

1.18 Base-lines for theoretical predictions about the behaviour expected for a solution consisting of free ions only, Debye-Hückel and Fuoss-Onsager theories and the use of Beer's Law

1.18.1 Debye-Hückel and Fuoss-Onsager equations

Setting up base-lines presupposes that it is known exactly how a solution consisting of free ions only would behave over a range of concentrations, and it is precisely here that problems arise. The theory behind the setting up of base-lines for the Debye-Hückel and Fuoss–Onsager theories is given in Chapters 10 and 12, and only the conclusions are summarised here.

The equations are:

$$\log_{10}\gamma_\pm = -A|z_1z_2|\sqrt{I} \qquad \text{Debye-Hückel limiting law} \qquad (1.9)$$

$$\log_{10}\gamma_\pm = \frac{-A|z_1z_2|\sqrt{I}}{1+B\dot{a}\sqrt{I}} \qquad \text{Debye-Hückel equation} \qquad (1.10)$$

$$\log_{10}\gamma_\pm = \frac{-A|z_1z_2|\sqrt{I}}{1+B\dot{a}\sqrt{I}} + bI \qquad \text{Debye-Hückel extended equation} \qquad (1.11)$$

$$\Lambda = \Lambda^0 - S\sqrt{c} \qquad \text{Fuoss-Onsager limiting law} \qquad (1.12)$$

$$\Lambda = \Lambda^0 - S\sqrt{c} + Ec\log_{10}c + Jc \qquad \text{Fuoss-Onsager extended equation} \qquad (1.13)$$

where:

I is the ionic strength,

Λ is the molar conductivity at finite concentrations,

Λ^0 is the molar conductivity at infinite dilution.

The constants A and B are defined in Section 10.6.16 and S, E and J are defined in Section 12.10.

In these equations, with the possible exception of Equation (1.11), all quantities on the right hand side are known or calculable, and in this respect these equations should be excellent as base-lines for predicting the behaviour of electrolyte solutions. These equations account for non-ideality resulting from long range coulombic interactions, and can be used to predict the behaviour expected for such a solution. Any deviation from this predicted behaviour is then interpreted as due to some process which is removing ions from solution. This could be incomplete ionisation for a weak acid, or formation of a complex or an ion pair or other equilibria. A comparison of the actual observed behaviour of the solution with that predicted after non-ideality has been considered often leads to a determination of an equilibrium constant for the process assumed to be occurring. This all presupposes that the equations correcting for non-ideality are valid.

These two base-lines are based on theories which are conceptually very similar, and deal directly with non-ideality resulting from coulombic interionic interactions.The third base-line is totally different conceptually. It is based on Beer's law which describes the intensity of absorption of radiation by a solution as a function of concentration. It does not deal with non-ideality, and assumes that non-ideality of the coulombic interaction type has no effect on the theoretical expression.

1.18.2 Beer's Law equation

Spectroscopic and spectrophotometric methods are a standard way of identifying equilibrium processes and ascribing equilibrium constants to them. These methods are based on absorption of radiation by the species present in solution. The technique can be described qualitatively by saying that:

- The position of the lines in the spectrum gives the nature and identity of the absorbing species.

- The intensity of the lines gives the concentration of the absorbing species.

The intensity and the concentration are related by Beer's law which is the base-line for electrolyte studies by spectroscopic techniques.

$$\log_{10}\frac{I_0}{I} = A = \varepsilon c d \tag{1.14}$$

where I_0 is the incident intensity,

I is the intensity of the radiation transmitted,

A is the absorbance of the solution, and is directly measured by the instrument,

ε is a constant of proportionality – the molar absorption coefficient – and this depends on the nature of the absorbing species,

c is the concentration of the absorbing species,

d is the path length through which radiation is transmitted.

A and ε depend on the wavelength of the radiation used.

It is generally accepted that Beer's law is valid over most experimental concentrations. Deviations from the predicted values are interpreted as due to removal of the absorbing species by some equilibrium process, and a value for the equilibrium constant can be calculated.

Spectroscopic methods are also used to study equilibria in solution where **new peaks** are obtained when an equilibrium process is set up in solution. Observation of a **new peak** is indicative of a **new species** being formed, and study of that new absorption using Beer's law should generate an equilibrium constant. Spectroscopic methods can also help to distinguish between inner and outer-sphere associated species. For instance, there are theoretical and experimental reasons for assuming that:

- The visible spectrum picks up **inner-sphere** ion pairs and complexes.
- The UV spectrum picks up **outer-sphere** ion pairs and complexes.

One advantage of this method is that the deviations from expected Beer's law values are not attributable even in part to non-ideality, but are totally due to the setting up of an equilibrium process, in contrast to activity and conductance methods where deviations may be due to unaccounted for non-ideality plus association.

1.19 Ultrasonics

This technique has been used to determine association constants for equilibria in electrolyte solutions, particularly for ion association. It has also been used to study solvation effects on ion association (see Section 13.10.5).

A sound wave is passed through an electrolyte solution in which there are species present at equilibrium. This is done over a range of frequencies of the sound wave, and the absorption of sound energy by the solution, or the velocity of the sound wave is measured for each frequency. The sound wave is equivalent to a pressure wave or to a series of alternating temperatures, and these call for a corresponding **wave of new equilibrium positions to be set up**.

If the concentrations of the species present in solution can alter rapidly enough then **each new equilibrium position can be set up** as each new temperature is attained. When this happens, the equilibria and the concentrations can keep in phase with the periodic displacement of the sound wave and there is no great change in the velocity or absorption of the wave.

If reaction does not happen fast enough, then the concentrations of the species present will not alter with the periodic displacement and the **required new equilibrium positions are not set up**. Again the absorption of energy or the velocity of sound will not alter much over a range of frequencies.

If, however, the concentrations can alter rapidly enough, and the new equilibrium positions can be set up but are **out of phase** with the periodic displacement of the sound wave, then this shows up as an increase in the velocity of the sound wave, or as a dramatic increase in the absorption of sound (see Figure 1.2(a) and (b)). Each time this happens an equilibrium process is adjusting itself. The **number of times** this happens shows directly the **number of equilibrium processes** occurring in the solution which are being disturbed by the sound wave (see Figure 1.2(c) and 1.2(d)). Sometimes two or more peaks are superimposed, but these can be resolved by standard curve-fitting techniques.

The beauty of the ultrasonic method lies in this possibility of picking out how many equilibrium processes are present, and multistep equilibria can often be disentangled with relative ease. This is something which the other methods are either incapable of, or which they can only do with difficulty and ambiguity.

However, there still remains the fundamental problem of identifying the process chemically. Identification of the process in the chemical sense is ambiguous as there is no direct chemical observation of the system. It is easy to distinguish between chemical processes and physical processes, such as ion–solvent interactions or energy transfer, by the frequencies at which the maxima in the absorption of sound occurs. Identification of the chemical equilibria and the chemical species present are inferred through a fit of theory plus inference with experiment, and the data may be susceptible to more than one interpretation. One clue which has been used is that the frequency at which absorption of

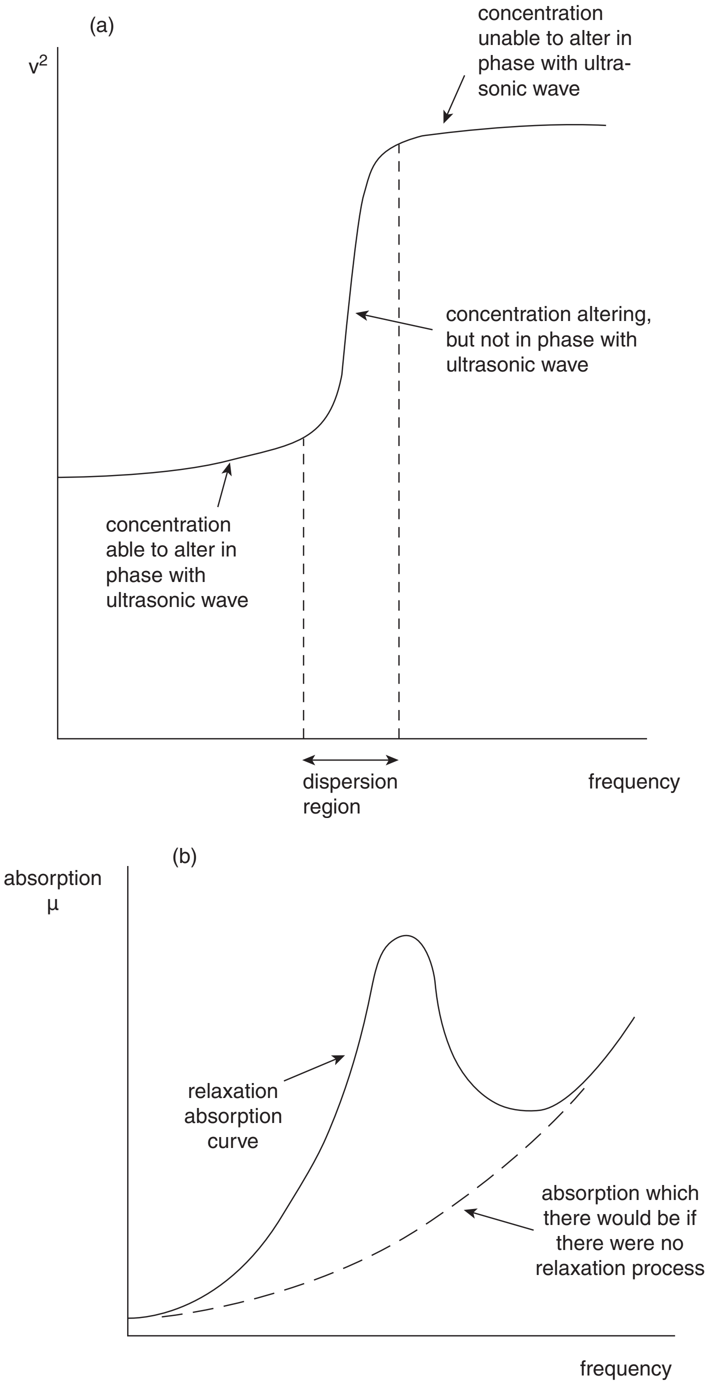


Figure 1.2 (**a**) Periodic relaxation diagram showing the dependence of the velocity of an ultrasonic wave on frequency for one equilibrium; (**b**) periodic relaxation diagram showing the dependence of the absorption of an ultrasonic wave on frequency for one equilibrium; (**c**) periodic relaxation for a double equilibrium: diagram for velocity of wave; (**d**) periodic relaxation for a double equilibrium: diagram for absorption of wave.

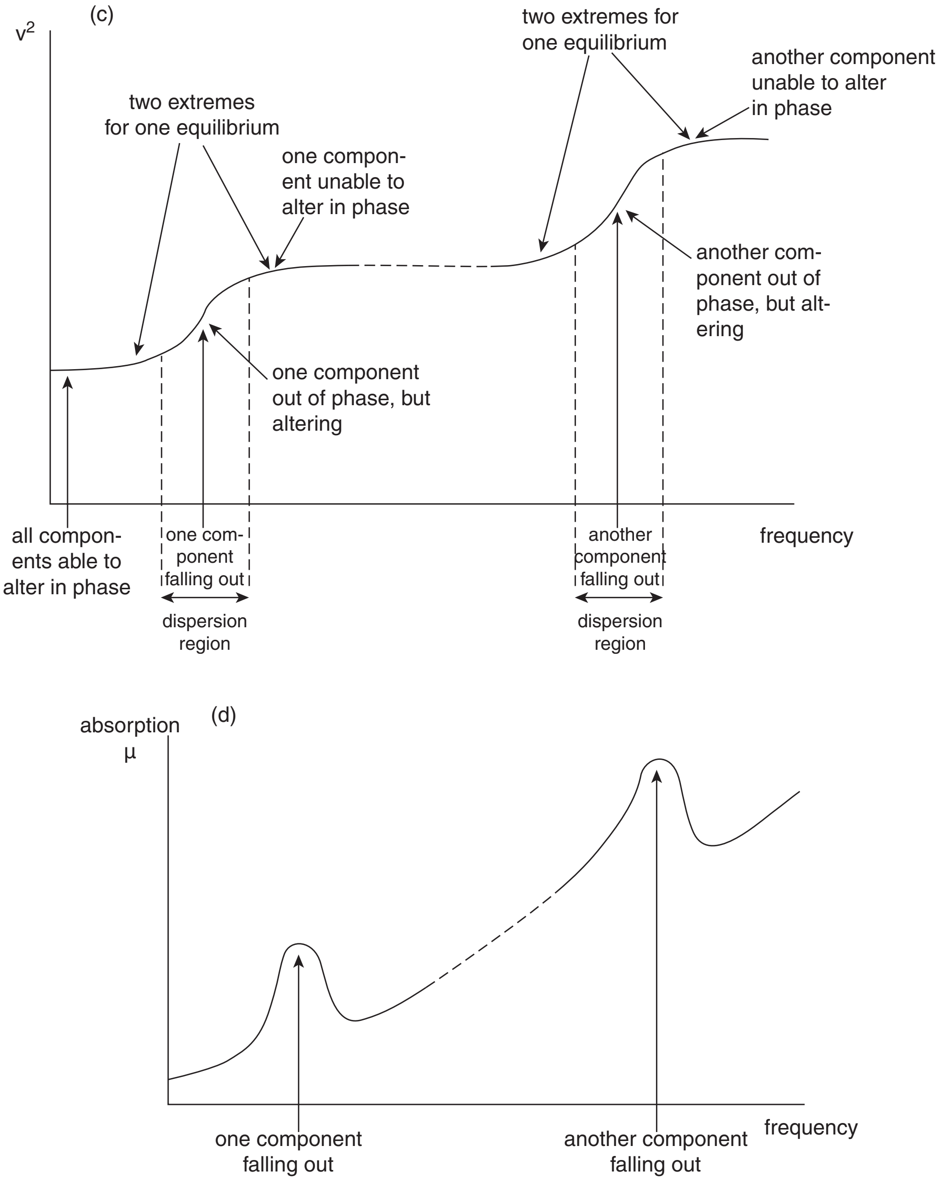


Figure 1.2 (*Continued*)

the sound wave occurs is related to the rate constants for the processes involved. This means that fast processes are more likely to involve ionic processes rather than covalent interactions. One other clue allows distinctions to be made between inner and outer-sphere species. If the frequency at which the maximum in the absorption of sound is found is independent of the nature of the cation, an outer-sphere species is involved. When solvent molecules separate ions, this means that the nature of the cation has less effect. If the frequency depends on the nature of the cation, then an inner-sphere species is involved.

However, inference and chemical knowledge are still the main basis for attributing a particular type of chemical process to a given absorption.

1.20 Possibility that specific experimental methods could distinguish between the various types of associated species

This will be discussed where appropriate throughout the book and below, but it is worthwhile issuing a word of caution here when assessing the likely success in making such distinctions. In fact, no technique has yet been devised which will enable an **unambiguous** and **categorical** distinction to be made between the various possible types of associated species. Claims that a technique can do so must have the evidence critically assessed. Ultrasonics and spectroscopic methods probably allow a distinction to be made with reasonable certainty between outer and inner-sphere ion pairs, while conductance work and scattering of light experiments allow micelle formation to be picked up very easily, but these are quite exceptional achievements in the field of association. Inferences made from thermodynamic and kinetic experiments have often been used, but they rely very heavily on being able to predict a model for the ideal solution – a topic fraught with difficulties as will be seen when the theories of electrolyte solutions are discussed.

1.21 Some examples of how chemists could go about inferring the nature of the species present

Various examples will be given throughout the book, and the following is only a brief survey with highly selective coverage, the main idea being simply to **illustrate** how to go about using experimental results to infer something about the chemical nature of the solution being studied. It would be useful to keep these examples in mind as the more theoretical aspects of electrolyte solutions are being developed.

(i) A combined spectroscopic and K_{assoc} magnitude example

- The association constants for equilibria involving $Co^{2+}(aq)$ with $SO_4^{2-}(aq)$ and $S_2O_3^{2-}(aq)$ are very similar:

$$K_{CoSO_4} = 2.3 \times 10^2\ \text{mol}^{-1}\ \text{dm}^3. \quad K_{CoS_2O_3} = 1.2 \times 10^2\ \text{mol}^{-1}\ \text{dm}^3.$$

Inference: The associated species are of very similar nature and are likely to be ion pairs since formation of an ion pair is influenced mainly by the charges on the associating species which are the same here.

- Both species show changes in the UV absorption, but formation of the thiosulphate associated species gives a change in the visible spectrum while formation of the sulphate does not.

Inference: $CoSO_4(aq)$ is an outer-sphere solvent-separated ion pair; CoS_2O_3 is an inner-sphere contact ion pair.

(ii) Ultrasonic studies

Sulphates of $Ni^{2+}(aq)$, $Mg^{2+}(aq)$, $Ca^{2+}(aq)$, $Mn^{2+}(aq)$, $Co^{2+}(aq)$, $Al^{3+}(aq)$, $Zn^{2+}(aq)$, $Be^{2+}(aq)$ give two absorption maxima, with the high-frequency maxima being independent of the nature of the cation, and the low-frequency maxima being dependent on the nature of the cation.

Inference: The following equilibria are set up:

$$\mathrm{M^{2+}(aq) + SO_4^{2-}(aq) \underset{A}{\overset{\text{diffusion}}{\rightleftharpoons}} (M^{2+}(H_2O)_2SO_4^{2-})(aq)}$$

outer-sphere solvent-separated ion pair

$$\mathrm{\underset{B}{\rightleftharpoons} (M^{2+}(H_2O)SO_4^{2-})(aq) \underset{C}{\rightleftharpoons} (M^{2+}SO_4^{2-})(aq)}$$

outer-sphere solvent-separated ion pair

inner-sphere contact contact ion pair

- Two maxima mean two equilibria to be identified. A is ruled out because diffusion is unlikely to give absorption of sound at the frequencies involved.

- The high-frequency maxima which are independent of the nature of the cation suggest that both species are solvent separated. This suggests that equilibrium B is involved here.

- The low-frequency maxima which are dependent on the nature of the cation suggest that the equilibrium involves a species with no solvent between the ions. This suggests that equilibrium C is involved here, since in this equilibrium the last H_2O molecule is being expelled to give the contact ion pair.

(iii) Another spectroscopic example

When $SO_4^{2-}(aq)$ is added to a solution containing $[(Co(NH_3)_5H_2O)]^{3+}(aq)$, a slow process is observed in the visible spectrum, and an immediate very rapid change is noted in the UV spectrum.

Inference: Two equilibria are involved:

$$\mathrm{[(Co(NH_3)_5H_2O)]^{3+}(aq) + SO_4^{2-}(aq) \overset{A}{\rightleftharpoons} [\{Co(NH_3)_5\}^{3+}SO_4^{2-}](aq) + H_2O(l)}$$

$$\mathrm{or\ [Co(NH_3)_5SO_4]^{+}(aq) + H_2O(l)}$$

$$\mathrm{[(Co(NH_3)_5H_2O)]^{3+}(aq) + SO_4^{2-}(aq) \overset{B}{\rightleftharpoons} [\{Co(NH_3)_5H_2O\}^{3+}solvent\ SO_4^{2-}](aq)}$$

- The slow change in the visible spectrum is attributed to equilibrium (A). A change in the visible spectrum suggests formation of a contact ion pair $[\{Co(NH_3)_5\}^{3+}SO_4^{2-}]$ (aq) or a complex ion $[Co(NH_3)_5SO_4]^{+}(aq)$. A slow change suggests formation of a complex with replacement of H_2O by SO_4^{2-}. This would mean an intimate chemical rearrangement involving covalent bonds.

- The fast change in the UV spectrum is attributed to equilibrium (B). Change in the UV spectrum suggests an outer-sphere solvent-separated species. A fast change would suggest a simple physical formation of an ion pair.

(iv) Use of Bjerrum's theory

Bjerrum's theory (Section 10.12) deals explicitly with formation of ion pairs, and can be used to calculate an expected value for the association constant for an equilibrium between two ions and an ion pair. This predicted value can be compared with the observed value.

The conclusions are:

- If the two values are similar, then it is likely that ion pairing is involved since Bjerrum's theory deals explicitly with short-range coulombic interactions which are predominantly dependent on the charges on the ions.

- If $K_{\text{observed}} \gg K_{\text{Bjerrum}}$, then it is likely that complexing is involved since a much larger K_{assoc} would suggest additional interactions over and above those involved in Bjerrum-type association which is dependent on electrostatic interactions only. The differences between the observed and predicted values would have to be sufficiently large for them not to be easily attributable to inadequacies in the theoretical base-line for analysing the data, or in the derivation of the Bjerrum equation itself.

(v) Application of thermodynamic reasoning

Most of these methods are based on correlations of the observed equilibrium constant with properties like: atomic number of the cation, type of cation, type of anion, type of ligand, pK of the ligand if it is a weak acid or weak base, crystallographic radii, solvated radii, electrostatic interaction energies, ionisation energies of the cation, symmetry of the ligand and more exotic properties.

Ion association can be described as:

$$\mathrm{M}^{n+} + \mathrm{A}^{m-}(\mathrm{aq}) \rightleftharpoons \mathrm{MA}^{(n-m)+}(\mathrm{aq})$$

$$K_{\text{assoc}} = \left(\frac{[\mathrm{MA}^{(n-m)^{+}}][\gamma^{(n-m)^{+}}}{[\mathrm{M}^{\mathrm{n}+}]\gamma^{\mathrm{n}+}[\mathrm{A}^{m-}]\gamma^{m-}}\right)_{\text{equilib}} \tag{10.15}$$

$$\text{with } \Delta G^{\theta} = -RT\log_{e}K_{\text{assoc}} \tag{10.16}$$

$$\text{since } \Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta} \tag{10.17}$$

$$\log_{10}K_{\text{assoc}} = -\frac{\Delta H^{\theta}}{2.303RT} + \frac{\Delta S^{\theta}}{2.303R} \tag{10.18}$$

Equations 10.17 and 10.18 show up the fundamental flaw in any such correlation. ΔG^{θ} and hence K_{assoc} are composite quantities, and values of ΔG^{θ} or K_{assoc} could be very similar for different systems **simply** because variations in ΔH^{θ} and ΔS^{θ} **compensate out**. Care must be taken to ensure that this is not the case. This is especially so when the conclusions from the experimental data depend crucially on the magnitude of ΔG^{θ} (or K_{assoc}), or on an observed variation of ΔG^{θ} or K_{assoc} with properties such as those listed above. Ideally both K_{assoc} and

$\Delta H^{\theta}_{\mathrm{assoc}}$ should be measured and from this $\Delta S^{\theta}_{\mathrm{assoc}}$ can be found. Modern precision calorimetric data allow highly accurate values of $\Delta H^{\theta}_{\mathrm{assoc}}$ to be found and in turn this can lead to very accurate $\Delta S^{\theta}_{\mathrm{assoc}}$ values.

This fundamental problem is one which has also been shown to be of supreme importance when solvation is being considered.

However, unless both ΔG^{θ} (or K_{assoc}) and $\Delta H^{\theta}_{\mathrm{assoc}}$ are measured, then the experimenter is forced into using the old correlation methods. Useful information can be obtained provided the interpretation is not pushed too far.