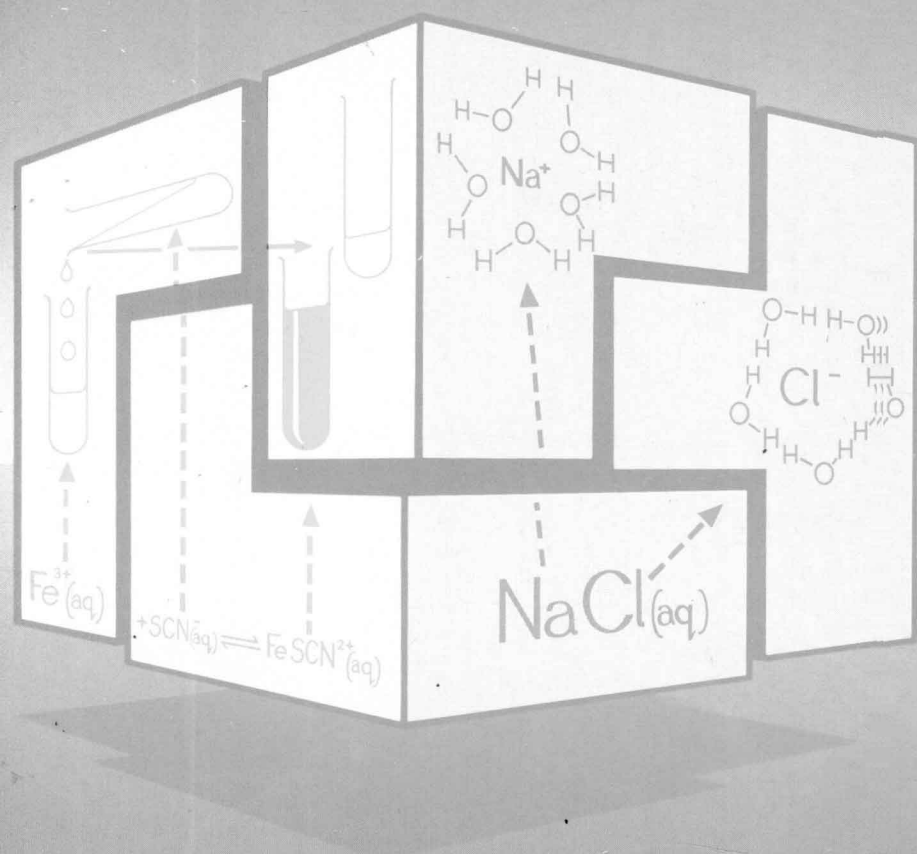


The Nature of Electrolyte Solutions

Margaret Robson Wright



Dimensions of Science

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THE NATURE OF ELECTROLYTE SOLUTIONS

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THE NATURE OF ELECTROLYTE SOLUTIONS

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*In gratitude to my husband Patrick,
and also to
Andrew, Edward and Anne
and the cats*

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Series Editor's Preface

This book is one in a Series designed to illustrate and explore a range of ways in which scientific knowledge is generated, and techniques are developed and applied. The volumes in this Series will certainly satisfy the needs of students at 'A' level and in first-year higher-education courses, although there is no intention to bridge any apparent gap in the transfer from secondary to tertiary stages. Indeed, the notion that a scientific education is both continuous and continuing is implicit in the approach which the authors have taken.

Working from a base of 'common core' 'A'-level knowledge and principles, each book demonstrates how that knowledge and those principles can be extended in academic terms, and also how they are applied in a variety of contexts which give relevance to the study of the subject. The subject matter is developed both in depth (in intellectual terms) and in breadth (in relevance). A significant feature is the way in which each text makes explicit some aspect of the fundamental processes of science, or shows science, and scientists, 'in action'. In some cases this is made clear by highlighting the methods used by scientists in, for example, employing a systematic approach to the collection of information, or the setting up of an experiment. In other cases the treatment traces a series of related steps in the scientific process, such as investigation, hypothesising, evaluation and problem-solving. The fact that there are many dimensions to the creation of knowledge and to its application by scientists and technologists is the title and consistent theme of all the books in the Series.

The authors are all authorities in the fields in which they have written, and share a common interest in the enjoyment of their work in science. We feel sure that something of that satisfaction will be imparted to their readers in the continuing study of the subject.

Preface

Information about what goes on at the molecular level in an electrolyte solution tends not to be taught as an independent topic at the introductory level, but to appear incidentally in books which are essentially about electrochemistry. By electrochemistry I mean treatments which cover such topics as electrolysis, electrochemical cells, EMFs, weak acids and bases, conductivity, transport numbers and so forth. These treatments will normally cover basic theory and experimental techniques.

This book, on the other hand, is about the chemical species which are present in an electrolyte solution, and about the ideas which explain the properties and behaviour of electrolyte solutions at the molecular level. Of necessity, we are drawing on information derived from standard electrochemistry, and basic A-level knowledge of this subject is assumed in this book. However, as will become apparent in progressing through the book, thinking about the meaning of experiments on electrolyte solutions, and the interpretation of these experiments in terms of the nature and the behaviour of the solutions, requires drawing on information from branches of chemistry other than electrochemistry proper.

The nature of electrolyte solutions is not just a matter of interest only to electrochemists. A knowledge and understanding of what goes on in electrolyte solutions is vitally important to other chemists and scientists. For instance, many solution kineticists have to be as versatile and knowledgeable in electrolyte solution chemistry as they are in kinetics. Inorganic solution chemists would likewise limit themselves drastically if they did not have electrochemical ideas at their fingertips. And in the last decade or so it has become clear that electrochemical studies and concepts are becoming increasingly valuable and necessary in looking at many aspects of biological solutions.

This book, therefore, focuses attention on the current ideas about the nature and behaviour of the species present in aqueous electrolyte solutions. It also makes a very decided attempt to help and

teach students how to think for themselves, and so the reasoning and the logic behind the topics discussed is emphasised. This is done by showing them how practising chemists go about thinking about behaviour at the molecular level, and how we set about interpreting experimental results and tying them up with theory or results from other branches of chemistry. The book also tries to teach students how to be critical of interpretative thinking by showing the pitfalls into which we could slip if we take too dogmatic an approach or interpretation. Once these points have been explicitly made, it should be easier for the student to see how thinking about what is happening in aqueous solutions can lead to further ideas and consequent advances in our knowledge.

When this has been done for one topic, here electrolyte solutions, I would hope that the student could transfer these thinking processes to other aspects of chemistry, or indeed of science, and thereby become a better all-round chemist or scientist.

It is unfair to expect students to work all this out for themselves, over and above the very necessary learning of facts. It is the teacher's duty to show and to explain how to think scientifically. The philosophy behind this book is that this is best done by detailed explanation and guidance, and by direct illustration on a limited scope of topics. This book, therefore, is not comprehensive. But if the ideas and thought processes outlined in the book are carried over to other topics studied elsewhere the student should find that 'he can do it for himself' and thereby can gain much more satisfaction and confidence than he would by just learning facts. It is understanding, being able to see for oneself, and confidence which help to stimulate and sustain interest.

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Acknowledgements

This book is the result of the accumulated experience of over twenty very stimulating years of teaching students at all levels. During these years I learned that being happy to help, being prepared to give extra explanation and to spend extra time on a topic could soon clear up problems and difficulties which many students thought they would never understand. Too often teachers forget that there were times when they themselves could not understand and when a similar explanation and preparedness to give time were welcome. If, through the written word, I can help students to understand and to feel confident in their ability to learn, and to teach them in a book in a manner which gives them the feeling of a direct contact with the teacher, then this book will not have been written in vain. To all the many students who have provided the stimulus and enjoyment of teaching I give my grateful thanks.

My thanks are due to Professor R. J. P. Williams, F.R.S., for reading the whole manuscript and sending encouraging comments.

In particular, I would like to express my very considerable gratitude to Professor Felix Franks who made a very careful and thorough reading of the whole manuscript. He made many extremely helpful and invaluable comments. These have been taken into account in the final version of the book, but the contents are my responsibility alone.

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My husband, Patrick, has throughout my teaching career and throughout the thinking and writing of this book been a source of constant support and encouragement. His high intellectual calibre

and wide-ranging knowledge and understanding have provided many interesting and fruitful discussions. He has been an excellent sounding board for many of the ideas and manner of presentation in this book. He has read in detail the whole manuscript, and his clarity of insight and his considerable knowledge of the subject matter have been of invaluable help. My debt to him is enormous, and my grateful thanks are due to him.

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1 Concepts and Ideas

This book is about the nature and behaviour of electrolyte solutions. This will include studying the types of particles which are present in such solutions, and will require reviewing the experimental evidence from which we infer the structure and nature of both the solute and solvent species. We will also be looking at the ideas involved in the theories which describe the nature of electrolyte solutions as well as studying the development of those theories.

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 this out for you.

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 which are present in a solution. They can thus give us information about the number of particles **actually** present in the 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 particles 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 \longrightarrow 2 particles
CaCl₂(aq): 1 stoichiometric unit \longrightarrow 3 particles

and *this ratio does not alter with change in concentration* (see appendix A).

- (b) Those where the number of particles is greater than that corresponding to the stoichiometric unit, but is much less than the values found in category (a), such as ethanoic acid, CH₃COOH(aq), or ammonia, NH₃(aq). Here the ratio of the **actual number** of particles to the **stoichiometric number** of the stoichiometric units *increases dramatically with decrease in concentration* (see appendix A).

The electrical conductance of aqueous solutions has been studied. Some are **non-conducting**, some **weakly conducting** and some **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).

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

The solutes whose structures in the solid is a giant ionic lattice are those which give strongly conducting solutions and 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 solutions the solute can exist as

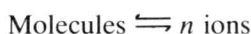
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| <p>(a) Molecular units: non-conducting, <i>normal</i> colligative properties, X-ray structure showing discrete molecular units in the solid.</p> <p>(b) Molecular units plus ions: weakly conducting, colligative properties showing slightly more than the expected numbers of particles present, X-ray structure showing discrete molecular units in the solid.</p> |
|--|

- (c) **Ions:** highly conducting, colligative properties considerably greater than expected, X-ray structure showing a giant ionic lattice.

Solutes giving in solution:

- (a) **Molecular units** are called **non-electrolytes**
 (b) **Molecular units plus ions** are called **weak electrolytes**
 (c) **Ions only** are called **strong electrolytes**

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



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

Determination of values of the equilibrium constant has been an important experimental study, with conductance and EMF methods being the main tools.

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 results in a dramatic increase in the molar conductance as the concentration decreases.

A **strong electrolyte** consists of ions with no significant amounts of molecular species present. We would expect that the molar conductance would be independent of concentration. (Molar conductance and related electrical quantities are given in appendix A.)

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

- (a) For **strong** electrolytes the molar conductance is **not** independent of concentration.
 (b) Electrolytes which are **strong** in **aqueous** solutions are shown to behave like **typical weak electrolytes** in **solvents** like **dioxan, acetone** or **methanol**.
 (c) These anomalies are reflected in other studies using strong and weak electrolytes.

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

- (i) 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?
- (ii) What exactly is the role of the solvent, and do we have to consider its **molecular** properties as well as its **bulk** properties?

I. IONS — SIMPLE CHARGED PARTICLES OR NOT?

Some simple basic properties of ions are regularly used in our discussion of electrolyte solutions and in theories describing the behaviour of electrolyte solutions. These ideas are often physically naive and we will find that we must modify them before we can ever hope to have a physically realistic description of electrolyte solutions.

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

Simple Properties of Ions

1. Ions have **integral** positive or negative charges.
2. Ions have finite definite sizes
— **but** see discussion below of **solvation**.
3. Ions are often considered to be spherically symmetrical
— **but** see discussion below of **shapes** of ions.
4. We normally consider the charge to be evenly distributed over the surface of the ion
— **but** see discussion below of **charge-separated** ions.
5. We normally talk of ions as being unpolarisable
— **but** see discussion below of **polarising power** and **polarisability**.
6. We normally think of each ion as moving as an independent entity
— **but** see discussion below of **ion-pairing** and **micelle clustering**.

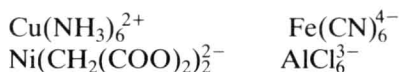
7. Ions can be ordered in terms of their ease of discharge at an electrode.
8. H^+ and OH^- in aqueous solutions show special properties.

Modifications needed to those 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 that 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 4. Knowledge about solvation of ions is vital to our 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 discussion of electrolyte solutions is based on an assumption that ions are spherically symmetrical, there is a tendency to forget that many ions are certainly not spherically 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-} and PO_4^{3-} are nearly spherically symmetrical, as are many of the complex ions found in inorganic chemistry:



but many organic ions are not:



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