Preface

It is so often stated that water is a ubiquitous liquid on earth and a general solvent for many kinds of solutes that such statements sound as clichés. Nevertheless, they are correct and merit discussion. Other common statements are that the properties of water are unique among liquids and are difficult to understand: "No one really understands water. It's embarrassing to admit it, but the stuff that covers two-thirds of our planet is still a mystery. Worse, the more we look, the more the problems accumulate: new techniques probing deeper into the molecular architecture of liquid water are throwing up more puzzles." (Ball 2008). Unfortunately, to date this situation keeps being rather true and should be accorded a more comprehensive treatment.

On the other hand, ions are found in a large variety of environments. These include a non-environment where the ions are isolated in vacuum, as generated for example in a mass spectrometer. Ions in a gaseous phase include clusters of ionized water vapour relating to cloud formation. Ions in condensed phases may occur in solids, whether crystalline or disordered (glasses) but also in liquids, including room temperature ionic liquids or molten salts at higher temperatures. In such condensed phases the ions are in close vicinity to one another with strong coulombic interactions between their charges that tend to order the ions (at least over short distances in liquids) with alternating positive and negative charges.

Ions also exist in liquid solutions in a variety of solvents, whether non-aqueous, aqueous, or mixed. When ions are placed in a solvent, by the dissolution of an electrolyte capable of extensive ionic dissociation, the properties of such solutions cannot be estimated simply as weighted sums of the properties of the individual components, solvent and ions. This results from the strong interactions between the ions and the solvent molecules, which merit intensive investigation in order to comprehend the properties of such solutions. The ions tend to be solvated in solution with a solvation shell around them, the solvent separating the ions from one another, their mutual distance apart depending on their concentration. For a binary electrolyte, consisting of one cation C and one anion A at a molar concentration c their average distance apart is inversely proportional to the cube root of the concentration: ${d^{\mathrm{av}}}_{\mathrm{C-A}} = (2cN_{\mathrm{A}})^{-1/3}$ (Marcus 2009). If each of the ions has one solvent molecule attached to it in the space between them, there is hardly space for a further solvent molecule between the solvated ions at a concentration of 1 mol per litre. Therefore, the

properties of dilute and mildly concentrated solutions differ considerably. Moreover, electrolyte solutions may be homogeneous but also colloidal dispersions and their properties vary from those in the bulk to those near surfaces. The interactions of ions at solution surfaces, whatever the phase at the other side of the surface—a gas, an immiscible liquid, a solid (e.g., an electrode), or dispersed colloidal particles (including biopolymers)—are also a subject that requires attention.

Both biological systems and their physiology are based on the water that is present in all living things, which is essential to life, as well as on solutions of ions in the water. Furthermore, these solutions exist in rather heterogeneous situations, in the vicinity of surfaces of organic substances that are partly hydrophilic and partly hydrophobic and which may carry charges on their ionisable groups. Therefore, the biophysical implications of such solutions are consequences of the above-mentioned interactions. There exists thus a wide spread of topics that should be dealt with in a book such as the present one.

The term "entropy", meaning "transformation" in Greek, was introduced by Clausius for this well known but perhaps less well understood thermodynamic quantity. This entity is often interpreted as "disorder" in a system, equivalent to "chaos", but also as "lack of knowledge" in terms of information theory (Ben-Naim 2008). It is the purpose of this book to fill the gap in ordered knowledge about the above mentioned topics of ions in water, and lead the reader from "chaos" to "cosmos", which means in Greek "order" and "harmony". Therefore, "from chaos to cosmos" is an apt subtitle for this book, in particular because ions in aqueous solutions relating to biophysical phenomena are classified as "chaotropic" or "kosmotropic". The justification of the use of these terms in the context of biological systems is critically assessed in this book. The author does not belong to the biophysics research establishment, hence his efforts to bring order to the use of such terms such as chaotropic and kosmotropic ions and the Hofmeister effect and series is like tilting at windmills. Still, he is confident that the suggestions made in this book may infiltrate into this establishment and might be accepted in the long run.

This book, being written by a single author, cannot be a comprehensive treatise on the subject of ions in water. It does present the author's physicochemical point of view, but is annotated with a large number of references to the original literature. In the present millennium already some 700 books have been published that have "water" in their title, but only very few have bearing on the present spread of problems. Some, indeed "ancient", books on aqueous electrolyte solutions, however, should be mentioned here, because they contain the physicochemical basis for the present discussions: the books by Harned and Owen (1958) and by Robinson and Stokes (1965). More recently the books by Conway (1981) and by Marcus (1985) and a special journal issue edited by Harding (2001) bear directly on the problems dealt with here. Other books are mentioned in the chapters dealing with the specific topics.

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