

# Preface

So many specific ion effects are described in literature in thousands of papers since the pioneering studies by Franz Hofmeister and his group in Prague, some 130 years ago. Theoretical work has been done over a century now, yet still the puzzle persists. What is the origin of the interactions of simple ions with water, other ions and solutes, and with interfaces, beyond electrostatics? Is it only the size and charge density or do dispersion forces play a major role? In what cases are the charge distribution and the geometry of ions important? Is the size dominating or is it the size plus polarisability?

Can we ever predict specific ion effects quantitatively and beyond empirical rules? Is it like long-term weather forecast or can we find some general principles behind it?

The fact that the so-called Hofmeister series exist is a sign that some generalisation should be possible. But there are several Hofmeister series, direct and reversed ones, or even bell-shaped, and they may change with temperature and ion concentration. All this seems to be hopelessly complicated, and part of the problem comes from apparently diverging experimental results.

As an example, we can consider the surface properties of a simple electrolyte solution as follows: the experimentally measured surface tension can be calculated, according to Gibbs' equation, as an integral over the ion profiles perpendicular to the surface from zero to infinite distance from the surface. However, some experiments mainly probe the first atomic and molecular layers near the surface. It was one of the major findings of the last several years that *locally* (close to an interface) accumulation of ions can occur, despite the fact that *globally* (integrated over a large distance) depletion is detected. Therefore the old perception that small ions are always pushed away from the interface turned out to be wrong. Ions can be attracted to the surface in the first layers, although the surface tension of the total solution is enhanced, compared to pure water.

So, one of the challenges now is to relieve the putative contradictions coming from different experiments that were formerly believed to probe the same properties. All the more, numerous sophisticated experiments were done over the last ten years, raising more questions than giving answers.

As far as interpretations, models, and theories are concerned, there has been a major step forward over the last ten years or so. It seems that this old topic becomes again fashionable among theoreticians. Computers are so much more powerful than they were twenty years ago, and significant new ideas came up, especially concerning the probable role of ion polarisabilities. We can be optimistic that in another ten years, the puzzle of ion specificity will ultimately be resolved. What we can say today is that there will not be only one parameter for one type of ion that describes its effect in all circumstances. There will be a map of different and subtly mixed interactions responsible for specific ion effects. Depending on the quantity and system discussed, these interactions are mixed in different ways. However, there will appear some generality, for example, for ion–protein interactions. It will be possible to predict salting-in and salting-out effects independently of denaturation effects, by just knowing the nature of the amino acid residues that are exposed to water and ions. It will be possible to predict the negative surface potential of water in the presence of ions, the surface active behaviour of acids and, perhaps, the secret of gas bubble–bubble coalescence in water as a function of salt composition.

All these will have a major impact on our understanding of processes and structures in living systems, as well as in technological applications. The prediction of phase equilibria in the presence of different salts can save a lot of money.

So should we wait another ten years before editing this book? I believe that the progress in the last few years is so significant that we can just start to draw a raw picture of specific ions effects. Of course, the different chapters will also present several contradictory points of views. Therefore, in the last chapter I will try to make a summary out of all this information showing what is commonly accepted today and what is still in debate, and I will also try to sketch what will probably be in the future.

In the introductory chapter, it seems worthy to make an attempt of a general overview. It is not intended to be done extensively, for many good reviews exist. It is rather the intention to show some exemplary

experimental results and theoretical approaches that illustrate the broad range of ion effects, and to give an impression of the main axes of thinking about them.

**Werner Kunz**  
Regensburg  
July 2009

## About Werner Kunz



Werner Kunz was born in 1960 in Krummennaab/Bavaria, Germany. He obtained his Ph.D. degree in Chemistry in 1988 at the University of Regensburg, Germany, working on *Vapour Pressure Measurements and Statistical-Mechanical Theories for the Determination of Thermodynamic and Structural Properties of Electrolytes in Acetonitrile and Methanol*, in the group of Prof. Dr. Josef Barthel.

He spent four years as a postdoctoral fellow with Prof. Pierre Turq at the Université Pierre et Marie Curie in Paris, France and in the Laboratoire Léon Brillouin, CEA, Saclay, France. In 1992 he got his french ‘habilitation’ working on the *determination of the structure and dynamics of solutions, especially with the help of neutron scattering experiments*. In the

same year he was assistant professor at the Université de Technologie de Compiègne (UTC), France and worked as a research fellow at the CEA, Saclay, France.

In 1993 he was appointed professor at the UTC, France. He worked there until 1997, studying especially liquids, solutions, microemulsions and emulsions with industrial interest. In 1995 he created a new series of post-graduate courses (D.E.S.S.) on complex liquids and colloids.

In 1997 he moved to the Universität Regensburg as full professor. He has been a programme coordinator for the European Master of Science in colloidal and formulation chemistry since 2004.

He received grants and fellowships from the State of Bavaria, the Studienstiftung des Deutschen Volkes, the Fonds der chemischen Industrie, the NATO, the European Community, and Elf Aquitaine.

Since 2000 he has been a corresponding member of the European Academy of Sciences and Arts (Paris, London).