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Coulombic Fluids

Bulk and Interfaces

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Preface

During the last decade, the number of publications on ionic liquids has increased nearly exponentially. Obviously, this reflects an enormous interest in these liquids and their potential applications. Among their most striking characteristics are the low melting points near room temperature and the extremely low vapour pressures in the liquid state. Furthermore, a large variety of ionic liquids can be synthesized and so their properties can be tailored depending on the chemical demands. Generally, they are composed of an organic cation and an inorganic or organic anion. Therefore, their bulk and interfacial properties are dominated by Coulomb or Coulombic interactions. By focusing on this characteristic, one expects some similarities with their classical counterpart, the molten salts such as alkali halides that have been studied intensively for quite some time. So, the question arises: What can we learn from molten salts which could help improving our understanding of ionic liquids? Such a comparison is one of the main motivations for writing this book. Points of particular interest in the bulk phase concern their microscopic structure, the phase behaviour and critical phenomena, solubilities and solvation characteristics, transport, and other physicochemical properties. Interfacial phenomena comprise adsorption, wetting, and spreading characteristics, the problem of the electric double layer in ionic media, and, more generally, the electrified ionic liquid/electrode interface as well as potential electrochemical applications, for instance, in electrocrystallization or electrowetting. With regard to interfaces, in particular, a reversal of the above question is of similar attraction for molten salts. Due to their low vapour pressures, several interfacial investigations employing ultrahigh vacuum can be performed with ionic liquids, but are difficult or not possible with molten salts at elevated temperatures. So, there is a productive influence in both directions. This potential for interface studies has been realized only recently.

A further objective of this book deals with the change of the interionic interaction and electronic structure in systems such as metal–molten salt solutions or fluid metals. By expansion of a fluid metal or its dilution by adding salt, the electronic screening of the Coulomb potentials can be reduced to such an extent that electrons become localized or trapped in the Coulomb well and a metal–nonmetal transition occurs. The characteristics of this electronic transition in the fluid state are treated for selected examples.

The focus of this book is on a comparative study of molten salts and ionic liquids and their bulk and interfacial physicochemical properties. Special attention is drawn to recent experimental work and results of computer simulations. In addition, the topic of electronic transitions in fluids has been included, which bridges the way from electron to ion conducting liquids. All these systems have in common a dominating Coulomb interaction and so may be classified as Coulombic fluids. The first book entitled 'Coulomb Liquids' appeared in 1984 by March and Tosi. Its main focus was on different theoretical aspects of liquids, especially liquid metals and molten salts. In this book, the emphasis is on experimental research of molten salts and ionic liquids and their possible electrochemical applications in nanotechnology. It addresses to scientists and engineers working in the field, to physicists and chemists, as well as to material scientists interested in soft condensed matter. An introduction into the basic concepts and a detailed description of some of the main experimental methods assist the interested graduate student to get a direct access to these new and promising liquids.

Many of the results presented in the following chapters are based on investigations by the author's research group mainly over the last two decades. So, I am pleased to acknowledge gratefully the valuable contributions of my former research students and co-workers. For outstanding collaboration over several years, I am particularly indebted to D. Nattland and Th. Koslowski, C.L. Aravinda, V. Halka, G.B. Pan, R. Tsekov, and A. Turchanin. Special thanks are due to F. Hensel who introduced me to the fascination of fluid metals. During the preparation of the text and figures of this book, I got valuable assistance by D. Rohmert-Hug and J. Szepessy to whom I am especially grateful. Last, but not least, it is my pleasure to thank my brother Max and my good friend Helmut who always kept an eye on my health.

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