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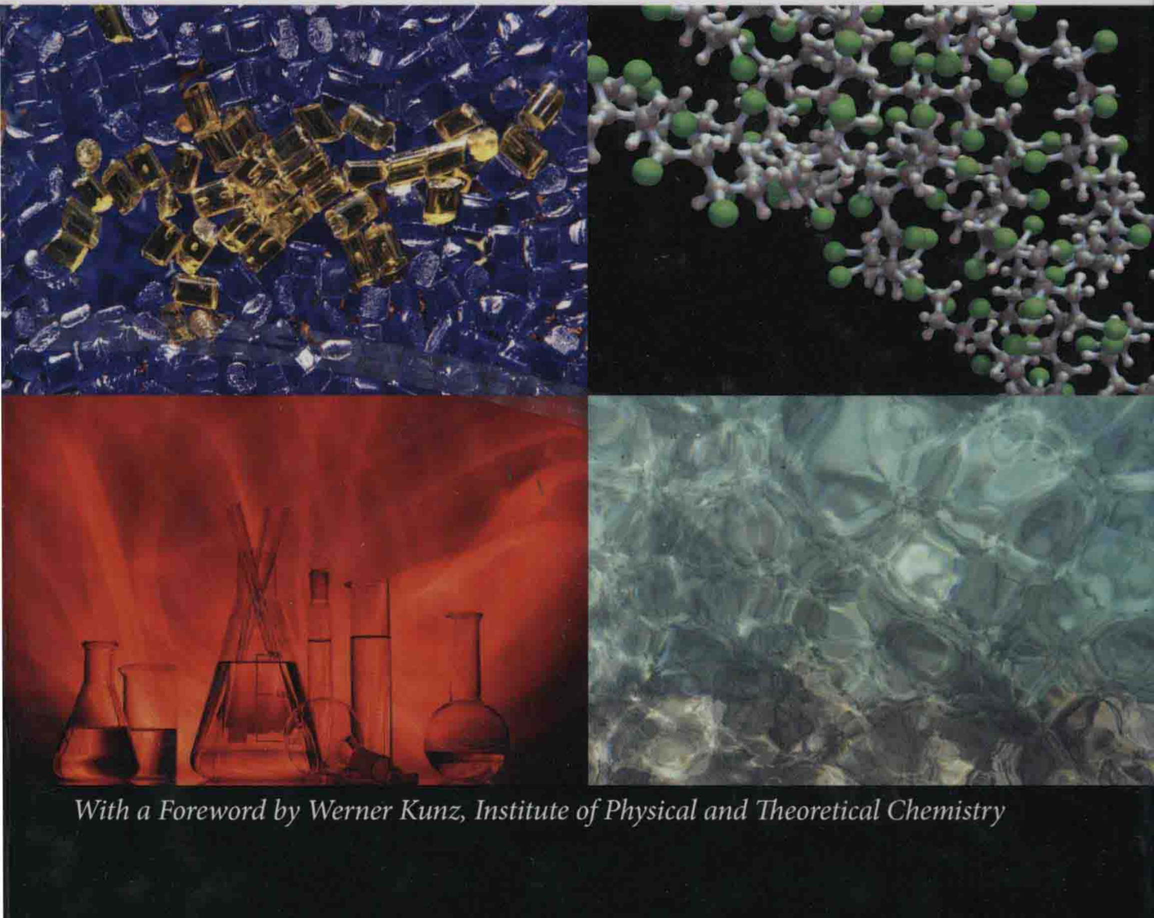
IONIC LIQUID-BASED SURFACTANT SCIENCE

Formulation, Characterization and Applications

Edited by **Bidyut K. Paul • Satya P. Moulik**



With a Foreword by Werner Kunz, Institute of Physical and Theoretical Chemistry

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FOREWORD

Over the last 15 or 20 years, the study of ionic liquids (ILs) has become very fashionable, and the published literature about these systems continues to grow exponentially. At the beginning of this voyage, it was argued that they are green, because their vapour pressure is negligible. However, it turned out that many of them are not green at all. This was recently discussed by Jessop in a landmark paper on the real needs in the field of green solvents [1]. He even concludes that the capacities of the ILs are overestimated, and too much efforts have been invested on their research.

Since the beginning of the widespread research on ILs, there has been another argument that they are "designer solvents," and can possibly be tuned to deliver any desired property. In the light of possible cation–anion combinations, there are possibilities of numerous products with melting points below 100°C, which is advantageous, especially for the scientists. We can publish thousands of articles, and since the community is ever growing, most of these papers will be highly cited. In return, the scientists have scope that in some decades all present unfavourable liquids will be replaced by the new ILs.

Of course, this is not realistic, and perhaps a big danger. It reminds me of all the promises made by electrochemists in the 1970s and 1980s. According to their views, conventional biofuel-driven cars should have been replaced by electro cars since many years. Everybody knows that they promised too much and that even a simple mobile phone must still be charged once a day. Therefore, we should be modest when speaking about so many "potential" applications of ILs. It is known now that most of them are not green, they are difficult to synthesize (and even more to purify), they often show high viscosities, and so forth.

So, is all bad with the ILs, and is the present monograph superfluous? Of course it is not. There is indeed a promising future for ILs, provided they are carefully chosen, and their properties and potential applications are compared with the existing systems so that their superiority can be proven. Or even better, that they fulfil tasks that could not be envisaged with current conventional liquids.

For the moment, I see the following advantages of ILs:

1. ILs are liquid over a considerable temperature range. For several applications that can be a significant advantage, for example in the field of nanoparticle synthesis at high or—even more—at very low temperature.

2. ILs contain a lot of charges. This is a disadvantage for the use of many enzymes, but it can be an advantage for electrochemical applications.
3. ILs can also be considerably surface active. And this is one of the main topics of the present monograph. Charged liquid surfactants are scarce, although not completely unknown in literature (indeed the so-called extended surfactants are liquid at room temperature [2]). But most of the classical charged surfactants are solid or delivered as dilute aqueous solutions. For applications, however, it is always better to work with liquids—they are easier to handle and it is not necessary to overcome the energy of crystallisation during mixing or dissolution. And there is a second advantage that is often overlooked. IL surfactants bear special charged headgroups, often with delocalised charges. This chemical specificity is interesting by itself. Not only is the special headgroup (like imidazolium, etc.) the main reason for the liquid state of the whole surfactant, but it can also deliver very special interfacial properties to the systems.

As shown and discussed in details in the present monograph, ILs can significantly modify the behavior of classical surfactants both in the bulk and at the interface. The obtained structures such as liquid crystalline ones can be similar to aqueous systems, but often the detected phases are significantly shifted to higher surfactant concentrations or, are even very different from their aqueous counterparts. The IL can be surface active on its own or in combination with classical surfactants. Surface-active ILs can undergo specific interactions with polymers and biomolecules, as well as with special chemicals, such as calixarenes. They may tune the activity of enzymes and can be used in separation science. Of special interest is their interaction with surfaces such as layered silicates. All these aspects—and some more—are treated in the first part of the book.

As far as colloidal chemistry is concerned, manifold applications could be interesting in this field, and several of them are discussed in this monograph. Within the liquid state, particularly microemulsions are considered, and this is the main topic of the second part of the book. Several scenarios are imaginable: the ILs serve either as base of the polar (pseudo-)phase or as apolar one or as surfactant interphase or as two of these phases or pseudo-phases [3, 4]. Until now, as far as I know, nobody mixed a polar, an apolar and a surface-active IL to get a solely IL-containing microemulsion. Water-free microemulsions are not new [5], but the variety is quite limited before ILs become available. This approach has a great promise, and could lead to a real fine-tuning of liquid nanoscopic environments leading to specially designed nano-reactors in chemical synthesis. Of course, it is mandatory to precisely know the structures of such microemulsions, and therefore several papers consider this topic from different angles. An attempt to calculate thermodynamic properties (densities) of ternary systems containing ILs is also presented.

As mentioned before, toxicity aspects are increasingly important. Not only in Europe and the United States it is very difficult to introduce new chemical substances to the market; if their toxicity (and non biodegradability) is significant, there is no future for them. Therefore, it is interesting to consider bio-based or at least biocompatible systems. They may be based on "drinkable" ILs or, as a similar type of systems, like, the deep eutectic solvents that have many points (positive and negative) in common with ILs, such as a high ionic strength and usually high viscosity.

This monograph has only covered selected aspects of the huge area of ILs. But I think that liquid IL-based surfactant systems and in particular IL-based microemulsions are a promising field where ILs could (finally) show their power so that "potential" applications may finally turn to real ones. But even without applications, fascinating new aspects of the liquid state of matter are found in this subject, and this, by its own, justifies the present efforts.

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PREFACE

Factually, ionic liquids (ILs) are both old and new. Although ethylammonium nitrate (EAN), an organic liquid of mp ≈ 14°C, is known since 1914 from the work of P. Walden, in recent years, ILs have received much attention as a class of neoteric nonaqueous solvents, because of their unusual properties, amply mentioned in this monograph. Functionalization of ILs by designing different cations and anions makes considerable room for flexibility in their properties, which qualify them to be termed "designer solvents." Studies on self-assemblies of conventional surfactants into micelles, vesicles, liquid crystals, and microemulsions in a variety of ILs have become an attractive field for both theoretical and applied research. Although significant literature (original papers and reviews) in this particular field are available in this decade to our knowledge, a comprehensive literature in the form of a book or monograph is yet to be published on IL-based self-assembled systems. Our endeavor is to fill this gap. In this book, we have attempted to provide a comprehensive presentation of the topics on the performance of IL-assisted micelles and microemulsions, discussing their fundamental characteristics and theories, and development of bio-ILs or greener biodegradable, non eco-toxic solvents. We comprehend that the book will be useful for advanced postgraduate and undergraduate students, researchers in institutes, universities, and industries. The landscape looks encouraging. Therefore, good-quality critical advancements in this field comprising prospective environment benign or greener IL-based self-assembled systems are expected to emerge in the coming years.

In Chapter 1, Murgia, Palazzo, and coworkers investigated the physicochemical behaviors of a binary IL $bmimBF_4$ and water, and the ternary NaAOT, water and $bmimBF_4$ mixtures essentially through the evaluation of the self-diffusion coefficients of the various chemical species in solution by PGSTE-NMR experiments. The diffusion of water molecules and $bmimBF_4$ ions were found to be within different domains, which suggested that the systems were nanostructured with formation of micelles having positive curvature and a bicontinuous micellar solution for the former and the later systems, respectively. The remarkable differences between the two systems are attributed to the specific counterion effect between the aforementioned ILs and the anionic surfactant. In Chapter 2, Bermudez and coworkers focused on the characterization of small (conventional surfactants) and polymeric amphiphiles (block copolymers) in different types of ILs (imidazolium, ammonium, phosphonium, etc.) with special reference to the interfacial and bulk behaviors, and compared them with aqueous systems to highlight similarities and dissimilarities between ILs and water as self-assembly media employing traditional techniques. Ultra-high vacuum (UHV) methods were also employed in the measurements. Possible applications and future directions of the studies on the fundamental behavior of amphiphiles at the interface and in the bulk have also been presented. In the Chapter 3, the self-assembly of nonionic surfactants (analogues polyoxyethylene alkyl ethers) in room-temperature ILs (RT-ILs) under varied physicochemical conditions emphasizing on different aspects, viz., thermodynamics of micellization, characterization of binary (surfactant-RT-ILs) phase behaviors, and adsorption characteristics at solid/RT–IL interfaces has been presented by Sakai and coworkers. In addition, the knowledge of the interfacial properties of RTILs with water in the absence and presence of non-ionic surfactants has been presented for a better understanding of the preparation mechanism of metal oxide particles in RT-ILs. A futuristic view concerning RT-ILs from the standpoint of colloid and interface chemistry has been addressed. In chapter 4, El Seoud and Galgano have made a detailed presentation on imidazole-derived IL-based surfactants (ILBSs; ILs with long-chain "tails"), including syntheses, determination of the properties of their solutions, comparison between their micellar properties and those of "conventional" cationic surfactants, for example, pyridine-based cationics, and their main applications. The authors have suggested that a single factor that distinguishes ILBSs from other conventional surfactants is their structural versatility. The most frequently employed schemes for the synthesis and purification of ILBSs are specified; in addition, the micellar properties (viz. the critical micelles concentration, counter-ion dissociation constant, surfactant aggregation number, thermodynamic parameters of aggregation) are also presented. The applications of the ILBSs are briefly discussed. The impact of ILs in terms of characterization of different types of interactions, they experience in the bulk and at the interface, has been addressed by Lopes and coworkers in Chapter 5, by taking into account three types of research work: self-aggregation behavior of dialkylpyrrolidinium bromide ILs in the bulk phase using isothermal titration calorimetry, energetics at the IL–air interface (using 1-alkyl-3-methylimidzolium bistriflamide homologous series of ILs over a wide temperature range) from surface tension measurements, and finally, characterization of the adsorption of ILs on solid substrates (viz., gold and glass) using quartz crystal microbalance with dissipation (QCM-D), and atomic force microscopy (AFM). The results yielded a fascinating picture of the complex surface behaviors of ILs at the solid/liquid interface. In Chapter 6, Xu and Zhou summarized the aggregation behavior of aqueous solution of IL-based gemini surfactants and their interactions with biomacromolecules (e.g., BSA, Gelatin, and DNA). These surfactants possess unique aggregation behaviors which have significant promise in industrial applications. Further, prospective applications, such as drug entrapment and release, gene transfection of IL-based gemini surfactants have been presented. Future directions of research on different aspects of IL-based gemini surfactants, including synthesis with new structure, understanding of the mechanism underlying interaction between these surfactants or with other substances, for example, polymers and biomacromolecules to develop their functional efficiency and application have been focused. In Chapter 7, Samanta and coworkers have presented the development of morpholinium ion-based ILs along with their physicochemical studies: these ILs have promise as potential benign (environment