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GUEST EDITORIAL

Ionic Liquids

It has been almost 10 years since Michael Freemantle wrote an article for *Chemical & Engineering News* entitled "Designer Solvents - Ionic Liquids May Boost Clean Technology Development"[1] and effectively launched a renaissance in scientific and engineering interest in both "salts" and "liquids". There are now in excess of 8000 papers (including over 900 patents or applications) that use the term "ionic liquid", over 97% of which have been published since Freemantle's article. With ever increasing academic and industrial interest, the field shows no signs of slowing down.

Ionic liquids are now being defined as salts composed solely of ions with melting points below 100 °C, although this strict definition is often given some latitude as more and more applications and insight arise from the increased scrutiny of heterogeneous liquids. While salts fitting this definition have been known for well over a century, the "ionic liquid phenomenon" appears to be sustained by the firm connection between fascinating fundamental science and increasingly diverse applications. Scientists and engineers from around the world have raced to prepare and characterize new combinations of ions that could meet the definition of an "ionic liquid" to try to predict physical properties from structure, and to use the more attractive accessible physical properties (e.g., non or low volatility; large liquidus ranges, etc.) in new applications.

The initial focus in the field has been on making use of the unique, tunable physical property set offered by ILs and their use as designer "green" solvents. This has led to early gross overgeneralizations both for and against the use of ILs. ILs have been declared everything from nontoxic, nonflammable, and nonvolatile to toxic, flammable, and volatile, statements that clearly can not be true for the entire range of possible compounds that meet the definition of an IL! It is the almost infinite variability of ion combinations that might lead to IL behavior that has been both a blessing and a curse. It has not yet proven possible to predict which ion combinations will lead to a given set of properties nor even whether they will lead to an IL.

With the increased attention from disciplines well outside chemistry and engineering, ILs are finding useful application in sensors, solar cells, solid-state photocells and batteries and as thermal fluids, lubricants, hydraulic fluids, and ionogels, to name only a few. Despite the fact that ILs today are defined by one physical property (melting point), many of the potential applications are now making use of combinations of chemical or biological properties, such as in the study of energetic or pharmaceutical ILs. ILs are indeed tunable, multipurpose materials for a variety of applications, rather than just solvents.

It is becoming increasingly clear that it is possible to form any specific IL composition depending on the user's needs and that the desired physical, chemical, and biological properties can be realized in a single salt by proper selection of the component ions or in mixtures of component ions. However, ILs, their interfaces, and their mixtures with other molecular species, such as water and carbon dioxide, are exceptionally complex systems. From a theoretical and molecular simulation perspective, these systems represent one of the greatest current challenges for accurate molecular modeling and, especially, for the capability to make *a priori* predictions of IL properties via computational methods.

In this special issue of *Accounts of Chemical Research*, 18 articles have been collected from a sampling of some of the leading IL research groups. The articles highlight the growing diversity within the field and the increasing level of fundamental knowledge being developed. On the experimental side, the solvent roots of the field are clearly evident with contributions discussing the characterization and use of ILs as solvents including detailed spectroscopic studies of solvent roles, dynamics, and local ordering. On the computational side, the articles highlight a growing, rapidly evolving, and increasingly predictive molecular

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simulation capability for ILs, ranging from *ab initio* electronic structure to atomistic molecular dynamics to coarse-grained modeling. These articles describe not only technical advances in our ability to accurately model these liquids but also a growing range of IL environments and behaviors beyond the "simple" bulk phase, such as interfaces, mixtures, unique self-assembly phenomena, spectroscopic properties, and spatial and dynamical heterogeneity. Notably absent, however, are contributions describing new theoretical developments in liquid state theory and statistical mechanics to help better characterize these complex systems. This surely represents an opportunity for the future, in addition to the need for continued development in predictive atomistic and coarse-grained molecular simulation capabilities.

The true power of the IL field will ultimately come from how we exploit our understanding of these modularly tunable liquid salts, and new knowledge and industrial technologies are already appearing. ILs have catalyzed interdisciplinary exploration of both properties and potential uses of ILs, new technologies, and quite a few new IL product lines from large and small chemical companies. The scope of liquid salts combined with the simplicity of design but complexity of understanding will continue to foster new research and the "ionic liquid phenomenon" should continue for quite some time.

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Reference

(1) Freemantle, M. *Chem. Eng. News* **1998**, *76* (30th March), 32.

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