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Topics in Current Chemistry

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Ionic Liquids

Volume Editor: Barbara Kirchner

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With a Foreword by Tom Welton

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Aims and Scope

The series *Topics in Current Chemistry* presents critical reviews of the present and future trends in modern chemical research. The scope includes all areas of chemical science, including the interfaces with related disciplines such as biology, medicine, and materials science.

The objective of each thematic volume is to give the non-specialist reader, whether at the university or in industry, a comprehensive overview of an area where new insights of interest to a larger scientific audience are emerging.

Thus each review within the volume critically surveys one aspect of that topic and places it within the context of the volume as a whole. The most significant developments of the last 5–10 years are presented, using selected examples to illustrate the principles discussed. A description of the laboratory procedures involved is often useful to the reader. The coverage is not exhaustive in data, but rather conceptual, concentrating on the methodological thinking that will allow the non-specialist reader to understand the information presented.

Discussion of possible future research directions in the area is welcome.

Review articles for the individual volumes are invited by the volume editors.

In references *Topics in Current Chemistry* is abbreviated *Top Curr Chem* and is cited as a journal.

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Foreword

"Ionic liquids will never find application in industry", "I don't understand this fad for ionic liquids" and "there is no widespread interest in these systems" are just three of quotes from the reports of referees for research proposals that I have received over the years. I wonder what these people think today. There are currently at least nine large-scale industrial uses of ionic liquids, including, we now recognise, the production of ε-Caprolactam (a monomer for the production of nylon-6) [1]. There has been a steady increase in the interest in ionic liquids for well over a decade and last year the number of papers and patents including ionic liquids was counted in the thousands. This remarkable achievement has been built on the hard work and enthusiasm, first of a small band of devotees, but now of huge numbers of scientists all over the world who do not see themselves as specialists in ionic liquids.

The ionic liquids field continues to develop at an incredible rate. No sooner do I think that I am on top of the literature than it turns out that a whole new area of work has emerged without me noticing. Things that were once supposedly impossible in ionic liquids, such as measuring the ^{1}H NMR of solutes, are now widely applicable (see Chapter 8). Hence, collected volumes such as this are very welcome. This volume complements some other excellent texts, notably: "Electrodeposition in ionic liquids", edited by Frank Endres, Andy Abbott and Doug MacFarlane; "Electrochemical Aspects of Ionic Liquids" edited by Hiro Ohno; "Ionic liquids in Synthesis", edited by Peter Wasserscheid and myself and a recent collected volume of Accounts of Chemical Research.

As one looks back over the last few decades it is possible to see trends emerging in the ionic liquids that are used and the main foci of interest. Early chloroaluminate systems with potential electrochemical applications gave way to ionic liquids with more air stable anions, with interest moving on to chemicals synthesis and catalysis. Then came new systems with specific properties to use as Task Specific Ionic Liquids (see Chapter 3), or for dissolving biomass polymers (Chapter 10), or as engineering fluids of various types. A small number of papers have now appeared on mixtures of ionic liquids. The exciting thing about ionic liquids is that as each development has occurred it has been in addition to the previous activities and not a replacement for these.

Now that the usefulness of ionic liquids has been established there is a return to the study of their structures and physicochemical properties, so that these can be

manipulated to maximise the benefits that ionic liquids can give. The importance of this need for greater understanding of and insight into the fundamental properties is the common thread that passes through the Chapters in this volume (particularly Chapters 2, 4, 5, 6 and 9). For me, it is a delight to see. Not because this makes for great academic research, even though it does, but because this is the only way to ensure that the full potential of ionic liquids can be realised. We are also fortunate nowadays that powerful modern theory and modelling tools are available to give us greater insight into the structures and properties of ionic liquids (Chapter 7) than the largely qualitative approaches that were available in the past. Of course, one can do nothing without reliable and reproducible syntheses for ionic liquids, which are admirably covered in Chapter 1.

What does this presage for the future of research in ionic liquids? Of course, one should always be aware that thing that you are most likely to see in any crystal ball is your own reflection. However, I do hope that the drive to understand how ionic liquids interact with solute materials to change their behaviour will continue. It would also be great to be able to truly realise the 'designer liquid' aspect of ionic liquids and to be able to produce an ionic liquid with any particular desired property by designing the ions *in silico* without having to make a library of variants. The work that is described in this volume is the first step on this path, but there is a very long way to go to this journey's end. My guess is that the most interesting developments will come from those who do not currently use ionic liquids, but will one day realise that they have a problem that an ionic liquid can solve. The truth about the future, as the proposal reviewers who produced the comments above should have known, is that nobody knows what is coming. That's what I like best about it.

London, Summer 2009

Professor Tom Welton
Imperial College London

Reference

Fábos, V.; Lantos, D.; Bodor, A.; Bálint, A.-M.; Mika, L. T.; Sielcken, O. E.; Cuiper, A.; Horváth, I. T. ChemSusChem, 2008, 1, 189

Preface

The discovery of ionic liquids can be dated back to the work of Paul Walden who was born in the Russian governorate of Livland on July 14th, 1863 and who worked out his thesis with Wilhelm Ostwald in Leipzig in 1891 under unusual circumstances. Among the many discoveries of Paul Walden, probably the most important ones are the Ostwald-Walden rule (1886: valency-conductivity relationship), the Walden inversion (1895: the inversion of the C-Atom for substitution reactions), Walden's viscosity rule (1906: constant product for viscosity and conductivity), Walden's rule (1909: molar volume at the boiling point) and the discovery of ionic liquids as reported in the article "Über die Molekulargrösse und elektrische Leitfähigkeit einiger geschmolzener Salze"("About the molecular size and electrical conductivity of some molten salts") [P. Walden, Bull. Acad. Imper. Sci. (St. Petersburg) 1914, 8, 405]. Walden was looking for salts that are liquid at small amounts of surrounding heat in order to conduct his low-temperature-studies: "…sie (BK: wasserfreie Salze) boten die Möglichkeit dar, mit Hilfe der für gewöhnliche Temperaturen gebräuchlichen Methoden und Apparate alle Messungen durchzuführen." ("…they (water-free salts) made it possible to take all relevant measurements with the aid of the methods and apparatus for usual temperatures.").

Since then, studies of "molten salts" have seldom been concerned with ionic liquids in particular, until a renaissance of the interest in these kinds of liquids began to be registered in literature. In 1982 John Wilkes introduced tetrachloroaluminate ionic liquids based on 1-alkyl-3-methyl-imidazolium as cation [Wilkes et al. Inorg. Chim. Acta 21, 1263 (1982)]. The water and air-sensitivity of these substances led to what can be termed the second generation of ionic liquids when in 1992 the groups of Seddon, Hussey, and Chauvin suggested air- and water-stable ionic liquids through the replacement of moisture-sensitive $AlCl_4^-$ anion by BF_4^- and other anions [e.g. Seddon, Kinetics and Catalysis 37, 693 (1996)]. From 1998, Jim Davis and others introduced the third generation which sometimes is featured in literature under the term "designer solvents" or "task-specific ionic liquids" [Davis Jr. JH, et al., Tetrahedron Lett. 39, 8955 (1998)]. That these liquids were new solvents which cannot be understood merely as cases of some kind of molten salts has been made clear in no uncertain terms by Ken Seddon: "To use the term molten salts to describe these novel systems (BK: ionic liquids) is as archaic as describing a car as a horseless carriage" [Seddon, J. Chem. Tech. Biotechnol. 68, 351 (1997)]

Although a new class of solvents has emerged in the form of these ionic liquids, a systematic classification of them seems almost impossible. Whenever a new characterisation was discussed or a rule was phrased, some counter-example appeared out of the blue. When ionic liquids were sold as green solvents, this ran into trouble when they were shown to be fairly toxic [Ranke et al., Chem. Rev., 107, 2183 (2007)] and non-digestable. And while their low vapour-pressure seemed to point in the general direction of green solvents, it remains demonstrably true that some ionic liquids can be distilled [Earle et al., Nature 439, 831 (2006)]. Judging from the components of these solvents, namely ions, one would expect a high polarity for ionic liquids; however, these have been found [Wakei et al., J. Phys. Chem. B 109, 17028 (2006)] to be rather moderate and comparable to alcohols. Even the presence of pure ionicitiy was, after a while, questioned by scientists [Tokuda et al., J. Phys. Chem. B 110, 19593 (2006)] who found a relaxing electrostatics and increasing dispersion for ionic liquids with increasing chain length at the side group. The quest for a common rule has also, among other things, looked into the question of the unity charge of the ions. Contrary to what many had believed, it was recently explained by my colleague Koen Binnemans [http://www.kuleuven.be/cv/u0007851e.htm] that higher charged species form ionic liquids as well.

The importance of ILs is elucidated by many existing scientific programmes and labs, for example the Japanese "Science of ionic liquids" [http://ionliq.chem.nagoya-u.ac.jp/english/index.html], the Power, Environmental & Energy Research Center PEER [http://www.peer.caltech.edu/ionic.htm], the Queen's University Ionic Liquid Laboratories QUILL [http://quill.qub.ac.uk/], or the German priority programme "Ionic liquids" [http://www.dfg-spp1191.de] to name but a few, and several conferences are being conducted on this topic. It is furthermore illustrated by the fact that many books on the topic exist.

This volume contains a selection of some pointers on the important topics that are now discussed regarding ionic liquids. The main focus is on fundamental problems. In that sense, it really is a "topics in current chemistry"- volume, because it covers a topic of broad current interest (ionic liquids) in a way that gives the non-specialist reader a comprehensive overview.

The volume begins with a chapter by Bronya Clare, Amal Sirwardana and Douglas R. MacFarlane on synthesis and purification of ionic liquids. A good starting point for a substance consists in understanding its synthesis. However, for the class of ionic liquids, large alterations of their properties were observed when impurities are present, which is why a special emphasis has to be given to this issue. In the next chapter, Annegret Stark evaluates induced effects on organic reactions when ionic liquids are chosen as a solvent. One of the most promising opportunities in the field of ionic liquids consists in the possibility to modify ionic liquids to obtain functionality. Mathieu Pucheault and Michel Vaultier elaborate on this topic of task specific ionic liquids, with special emphasis on onium salts. The solubility and other features of heavy elements in ionic liquids are discussed by Andreas Taubert. The author concludes that the many remaining open questions are due to the sometimes complex behaviour of the metal ions in an already complex liquid and an even more complex interplay between the two. This is a fact that applies to many more solutes in ionic liquids.

How useful a solute can be as a probe is presented in the chapter by Margarida F. Costa Gomes, José N. Canongia Lopes and Agílio A. H. Pádua. In this chapter the thermodynamics and microhetergeity are illuminated from the perspective of molecular dynamics simulations. The subsequent chapter by David Rooney, Johann Jacqemin and Ramesh Gardas discusses the thermophysical properties of ionic liquids from an experimental point of view and evaluates the application of models as predictive tools. The difficulties and inherent virtues of some theoretical methods are discussed by me in the next chapter. When applying NMR techniquies, some difficulties are faced. In the next chapter Ralf Giernoth devotes some thoughts to this and provides an overview of how NMR spectroscopy is applied to solve questions of ionic liquid structure and dynamics. An alternative to NMR is optical spectroscopy and consequently this topic is discussed in a separate chapter by Anja Mudring. Again the topic of purity is emphasized. This time, optical purity lies at the heart of the discussion. The final chapter by Suzie Su Yin Tan and Douglas R. MacFarlane highlights the recent progress of biomass processing in ionic liquids. Perspectives on how biomass reactions are related to green chemistry, economic viability and other biomass productions are given.

As editor of the volume, I hope that this collection of fine articles reflects the current status of this important field of ionic liquids in a timely fashion, while at the same time highlighting possible future trends of the field which started because of a practical advantage and grew to such an important field. I would like to thank Fritz Vögtle and Markus Reiher as well as Tom Welton for their support in compiling this volume. To all the contributing authors I am indebted for providing this volume with such excellent and detailed chapters.

Leipzig, Summer 2009 Barbara Kirchner

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