

Ionic Liquids in Synthesis

Second, Completely Revised and Enlarged Edition

Volume 1

Edited by

Peter Wasserscheid and Tom Welton



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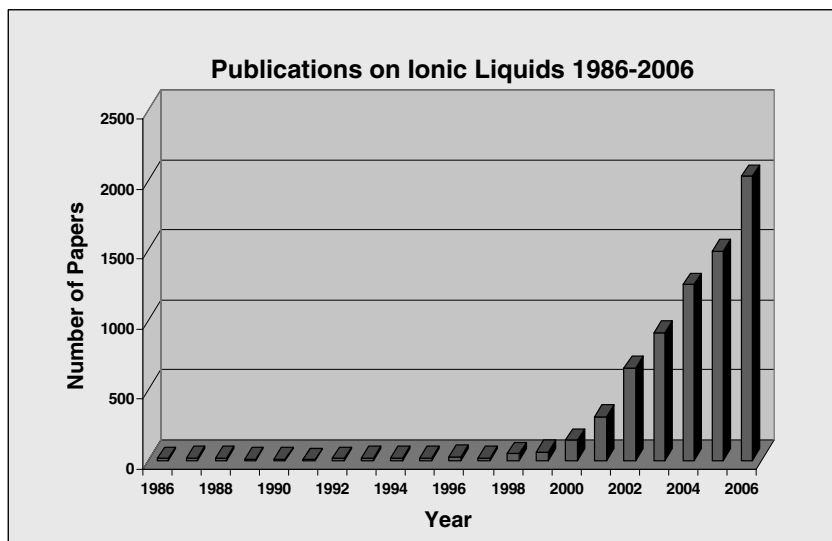
Preface to the Second Edition

“And with regard to my actual reporting of the events [. . .], I have made it a principle not to write down the first story that came my way, and not even to be guided by my own general impressions; either I was present myself at the events which I have described or else I heard of them from eye-witnesses whose reports I have checked with as much thoroughness as possible. Not that even so the truth was easy to discover: different eye-witnesses give different accounts of the same events, speaking out of partiality for one side or the other or else from imperfect memories. And it may well be that my history will seem less easy to read because of the absence in it of a romantic element. It will be enough for me, however, if these words of mine are judged useful by those who want to understand clearly the events which happened in the past and which (human nature being what it is) will, at some time or other and in much the same ways, be repeated in the future. My work is not a piece of writing designed to meet the taste of an immediate public, but was done to last for ever.”

*The History of the Peloponnesian War (Book I, Section 22),
Thucydides (431–413 BC), translated by Rex Warner*

Almost five years ago to this day, I wrote the preface to the first edition of this book (which is reproduced herein, meaning I don't have to repeat myself). I was honoured to be asked to do it, and it was an enjoyable task. How often do we, as scientists, get the privilege to write freely about a subject close to our hearts, without a censorious editor's pen being wielded? This is a rite of passage we more normally associate with an arts critic. So when Peter and Tom asked me to write the preface for the second edition, I was again flattered, but did wonder if I could add anything to what I originally wrote.

I was literally shocked when I read my original preface—was this really written only five years ago? How memory distorts with time! The figure illustrating the publication rate, for example—was it only five years ago that we were in awe of the fact that there was a “burgeoning growth of papers in this area”—when the total for 1999 was almost as high as 120! Even the most optimistic of us could not have anticipated how this would look in 2007 (see Figure 1). Approximately two thousand papers on ionic liquids appeared in 2006 (nearly 25% originating in China), bringing the total of published papers to over 6000 (and of these, over 2000 are concerned



with catalysis)—and there are also over 700 patents! That is 40 papers appearing per week—more than were being published annually a decade ago. And, on average, a review appears every two to three days. That means there is one review being published for every 20 original papers. If one assumes the garbage factor¹ runs at about 90% (a generous assumption), that means there is a review being published for every two valuable original contributions.

This is a bizarre and surreal situation, which seems more appropriate to a Kurt Vonnegut² novel—did buckminsterfullerene and superconductivity have the same problem? And how many papers within this annual flood of reviews say anything critical, useful, or interesting? How many add value to a list of abstracts which can be generated in five minutes using SciFinder or the ISI Web of Knowledge? How many of them can themselves be categorised as garbage? It is the twenty-first century—if a review is just an uncritical list of papers and data, what is its value?

So, am I being cynical and judgemental when I state that 90% of the published literature on ionic liquids adds little or no useful information? The PhD regulations for my University state that a satisfactory thesis must:

- (1) Embody the results of research which make a distinct contribution to scholarship and afford evidence of originality as shown by the discovery of new facts, the development of new theory or insight or by the exercise of independent critical powers; and
- (2) contain an acceptable amount of original work by the candidate. This work must be of a standard which could be published, either in the form of articles

¹ Discussed in the Preface to the First Edition.

² Sadly, he died in April 2007.

in appropriate refereed journals or as the basis of a book or research monograph which could meet the standards of an established academic publisher.

Well, clearly (2) is not evidence of (1); examination of the published literature undoubtedly demonstrates that “the results of research which make a distinct contribution to scholarship and afford evidence of originality as shown by the discovery of new facts, the development of new theory” is no longer a criterion for publication in refereed journals. If it was, would we find multiple publication of results from the same authors, or (frighteningly common) publication of work already published elsewhere by another, frequently uncited, group? Would papers on ionic liquids still be appearing where there is no report of the purity or water content of the ionic liquids, where claims of autocatalytic effects from the solvent appear based on reactions carried out in hexafluorophosphate or tetrafluoroborate ionic liquids (which contain HF), where physical properties are reported on impure materials, if the publications were properly refereed? I reject many of the papers which cross my (electronic) desk on these grounds when submitted to the ACS or RSC; months later I will see these papers appear, largely unchanged, in the pages of commercial journals—clearly, you can’t keep a bad paper down—publish, and be damned! I have actually heard scientists say “I can’t be expected to keep on top of the literature when it is appearing so rapidly.” Well, sorry, yes you can—it is your job and duty as a scientist to know the published literature. It has never been easier to keep up-to-date with the literature, but finding and downloading a .pdf file is not the same as reading it!! With 2000 papers appearing in 2006 (and will anyone bet against over 2500 in 2007?), we must exercise our critical faculties to the full; we must teach our students, colleagues and collaborators to look for experimental evidence, not unsubstantiated claims. The field of ionic liquids is vibrant, fascinating, and rewarding, and offers a phenomenal opportunity for new science and technology, but we must guard, as a community, against it getting a reputation (as green chemistry has already gained) for being an area of soft publications by mediocre scientists. And the attacks and carping criticism have started; Murray, in an editorial in the ACS journal *Analytical Chemistry* [*Anal. Chem.*, **2006**, *78*, 2080], rubbished both the areas of ionic liquids and green chemistry; although he later published a mealy-mouthed, insincere apology at the end of a response from Robin Rogers and myself [*Anal. Chem.*, **2006**, *78*, 3480–3481], it is clear that this will not be the last emotive, rather than logical, attack on the field. There are hundreds of outstanding papers being published annually in this area—they must not be tarnished by the hundreds of reports of bad science.

So, having vented my spleen, how do these rhetorical comments relate to this book, which has grown dramatically in size (but, thankfully, not to a size reflecting the growth of the number of publications) since the First Edition? The number of chapters and sections in the Second Edition reflect the broadening of the applications of ionic liquids; wherever a conventional fluid can be used, the option for replacing it with an ionic liquid exists. The present chapters are written from a depth of understanding that did not exist five years ago. Today, there are over a dozen extant industrial processes; in 2002, there were none in the public domain. This has been

achieved by ongoing synergistic collaborations between industry and academia, and not by the literally fantastic views expressed recently in an article entitled “Out of the Ivory Tower” [P.L. Short, *Chem. Eng. News*, **2006**, 84 (24th April)] [15–21]. The field has expanded and matured, and so has this Second Edition. The team of expert writers remains impressive—these are authors who are at the top of their field. The chapters radiate the informed writing of specialists; their wisdom is generously shared with us. The editors have performed a Herculean task in bringing this all together in a coherent and smooth account of the whole field as it stands today (although, at the current rate, the total number of papers published will rise above 10000 by 2009). If there is to be a Third Edition, and we will need one, it will have to be in two volumes! So let us hope this book is read by all practitioners of the field—by some for enjoyment, by all for insight and understanding, and by some as a bible. The field continues to expand and intrigue—by the time this book is in print, nearly one thousand more papers will have appeared—this textbook will remain the rock upon which good science will be built. To return to thoughts expressed over two thousand years ago, it will be enough “*if these words [. . .] are judged useful by those who want to understand clearly the events which happened in the past and which (human nature being what it is) will, at some time or other and in much the same ways, be repeated in the future. My work is not a piece of writing designed to meet the taste of an immediate public, but was done to last for ever.*”

K.R. Seddon
April, 2007

A Note from the Editors

This book has been arranged in several chapters that have been prepared by different authors, and the reader can expect to find changes in style and emphasis as they go through it. We hope that, in choosing authors who are at the forefront of their particular specialism, this variety is a strength of the book.

In addition to the subjects covered in the first edition we have added five new chapters describing newly emerging areas of interest for ionic liquids in synthesis. The book now ranges from the most fundamental theoretical understanding of ionic liquids through to their industrial applications.

In order to cover the most important advances we allowed the book to double in length. Yet, due to the explosion of interest in the use of ionic liquids in synthesis it has not been possible to be fully comprehensive. Consequently, the book must be didactic with examples from the literature used to illustrate and explain. We hope that no offence is caused to anyone whose work has not been included. None is intended.

Naturally, a multi-authored book has a time gap between the author's submission and the publication which can be different for different contributions. However, this was the same for the first edition of this book and did not harm its acceptance.

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We would like to sincerely thank everyone who has been involved in the publication of this book. All our authors have done a great job in preparing their chapters and it has been a pleasure to read their contributions as they have come in to us. We are truly grateful for them making our task so painless. We would also like to thank the production team at VCH-Wiley, particularly Dr. Elke Maase, Dr. Rainer Münz and Dr. Tim Kersebohm.

Finally in a project like this, someone must take responsibility for any errors that have crept in. Ultimately we are the editors and this responsibility is ours. So we apologize unreservedly for any mistakes that have found their way into this book.

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1

Introduction

John S. Wilkes, Peter Wasserscheid, and Tom Welton

Ionic liquids may be viewed as a new and remarkable class of solvents, or as a type of materials that has a long and useful history. In fact, ionic liquids are both, depending on your point of view. It is absolutely clear that whatever “ionic liquids” are, there has been an explosion of interest in them. Entries in Chemical Abstracts for the term “ionic liquids” were steady at about twenty per year through 1995, but grew to over 140 in the year 2000 and to more than 1500 in 2005. The reason for the increased interest is clearly due to the realization that these materials, formerly used for specialized electrochemical applications, may have greater utility as solvents for reactions and materials processing, as extraction media or as working fluids in mechanical applications, to name just a few of the more recent applications of ionic liquids.

For the purposes of discussion in this volume we will define ionic liquids as salts with a melting temperature below the boiling point of water. That is an arbitrary definition based on temperature, and says little about the composition of the materials themselves, except that they are completely ionic. In reality, most ionic liquids in the literature that meet our present definition are also liquids at room temperature. The melting temperature of many ionic liquids can be problematic, since they are notorious glass-forming materials. It is a common experience to work with a new ionic liquid for weeks or months only to find one day that it has crystallized unexpectedly. The essential feature that ionic liquids possess is one shared with traditional molten salts – a very wide liquidus range. The liquidus range is the span of temperatures between the melting point and boiling point. No molecular solvent can match the liquidus range of ionic liquids or molten salts, except perhaps some liquid polymers. Ionic liquids differ from molten salts just in where the liquidus range is in the scale of temperature.

There are many synonyms used for ionic liquids that complicate a literature search. “Molten salts” is the most common and most broadly applied term for ionic compounds in the liquid state. Unfortunately the term “ionic liquid” was also used to mean “molten salt” long before there was much literature on low melting salts. It may seem that the difference between ionic liquids and molten salts is just a matter of degree (literally); however the practical differences are

sufficient to justify a separately identified area for the salts that are liquid around room temperature. That is, in practice the ionic liquids may usually be handled like ordinary solvents. There are also some fundamental features of ionic liquids, such as strong ion–ion interactions that are not often seen in higher temperature molten salts. Synonyms in the literature for materials that meet the working definition of ionic liquid are: “room temperature molten salt,” “low temperature molten salt,” “ambient temperature molten salt,” and “liquid organic salt.”

Our definition of an ionic liquid does not answer the general question, “What is an ionic liquid?” This question has both a chemical and a historical answer. The details of the chemical answer are the subject of several subsequent chapters in this book. The general chemical composition of ionic liquids is surprisingly consistent, even though the specific composition and the chemical and physical properties vary tremendously. Most ionic liquids have an organic cation and an inorganic polyatomic anion. Since there are many known and potential cations and anions, the potential number of ionic liquids is huge. Discovering a new ionic liquid is relatively easy, but determining its usefulness as a solvent requires a much more substantial investment in determination of physical and chemical properties. The best trick would be a method for predicting an ionic liquid composition with a specified set of properties. That is an important goal that still awaits a better fundamental understanding of structure–property relationships and the development of better computational tools. I believe it can be done.

The historical answer to the nature of the present ionic liquids is somewhat in the eye of the beholder. The very brief history presented here is just one of many possible ones, and is necessarily biased by the point of view of just one participant in the development of ionic liquids. The earliest material that would meet our current definition of an ionic liquid was observed in Friedel–Crafts reactions in the mid-19th century as a separate liquid phase called the “red oil.” The fact that the red oil was a salt was determined more recently when NMR spectroscopy became a commonly available tool. Early in the 20th century some alkylammonium nitrate salts were found to be liquids [1], and more recently liquid gun propellants have been developed using binary nitrate ionic liquids [2]. In the 1960s John Yoke at Oregon State University reported that mixtures of copper(I) chloride and alkylammonium chlorides were often liquids [3]. These were not as simple as they might appear, since several chlorocuprous anions formed, depending on the stoichiometry of the components. In the 1970s Jerry Atwood at the University of Alabama discovered an unusual class of liquid salts he termed “liquid clathrates” [4]. These were composed of a salt combined with an aluminum alkyl, which then forms an inclusion compound with one or more aromatic molecules. A formula for the ionic portion is $M[Al_2(CH_3)_6X]$, where M is an inorganic or organic cation and X is a halide.

None of the interesting materials just described are the direct ancestors of the present generation of ionic liquids. Most of the ionic liquids responsible for the burst of papers in the last several years evolved directly from high temperature molten salts, and the quest to gain the advantages of molten salts without the disadvantages. It all started with a battery that was too hot to handle.