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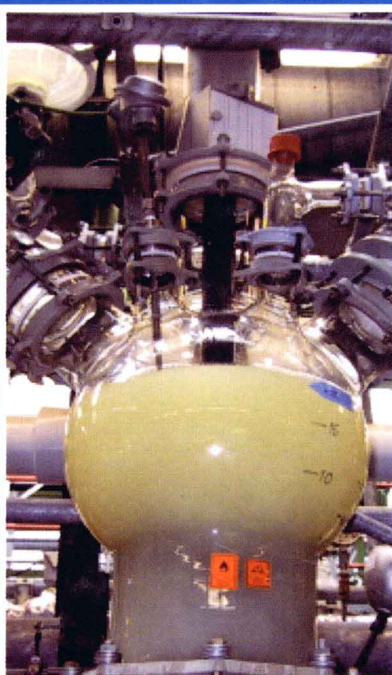

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Ionic Liquids in Synthesis

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Preface

"We prided ourselves that the science we were doing could not, in any conceivable circumstances, have any practical use. The more firmly one could make that claim, the more superior one felt."

The Two Cultures, C.P. Snow (1959)

A book about ionic liquids? Over three hundred pages? Why? Who needs it? Why bother? These aren't simply rhetorical questions, but important ones of a nature that must be addressed whenever considering the publication of any new book. In the case of this one, as two other books about ionic liquids will appear in 2002, the additional question of differentiation arises – how is this distinctive from the other two? All are multi-author works, and some of the authors have contributed to all three books.

Taking the last question first, the answer is straightforward but important. The other two volumes are conference proceedings (one of a NATO Advanced Research Workshop, the other of an ACS Symposium) presenting cutting-edge snapshots of the state-of-the-art for experts; this book is *structured*. Peter Wasserscheid and Tom Welton have planned an integrated approach to ionic liquids; it is detailed and comprehensive. This is a book designed to take the reader from little or no knowledge of ionic liquids to an understanding reflecting our best current knowledge. It is a teaching volume, admirable for use in undergraduate and postgraduate courses, or for private learning. But it is not a dry didactic text - it is a user's manual! Having established a historical context (with an excellent chapter by one of the fathers of ionic liquids), the volume describes the synthesis and purification of ionic liquids (the latter being crucially important), and the nature of ionic liquids and their physical properties. Central to this tome (both literally and metaphorically) is the use of ionic liquids for organic synthesis, and especially green organic synthesis, and this chapter is (appropriately) the largest, and the *raison d'être* for the work. The book concludes with much shorter chapters on the synthesis of inorganic materials and polymers, the study of enzyme reactions, and an overview and prospect for the area. This plan logically and completely covers the whole of our current knowledge of ionic liquids, in a manner designed to enable the tyro reader to feel confident in using them, and the expert to add to their understanding. This is the first book to attempt this task, and it is remarkably successful for two reasons. Firstly, the volume has been strongly and wisely directed, and is unified despite being a multi-author work. Secondly, the choice of authors was inspired; each one writes with authority and clarity within a strong framework. So, yes, this book is more than justified, it is a crucial and timely addition to the literature. Moreover, it is written and edited by the key people in the field.

Are ionic liquids really green? A weakly argued letter from Albrecht Salzer in *Chemical and Engineering News* (**2002**, 80 [April 29], 4-6) has raised this nevertheless valid question. Robin Rogers gave a tactful, and lucid, response, and I quote directly from this: "Salzer has not fully realized the magnitude of the number of potential ionic liquid solvents. I am sure, for example, that we can design a very toxic ionic liquid solvent. However, by letting the principles of green chemistry drive this research field, we can ensure that the ionic liquids and ionic liquid processes developed are in fact green. [. . .] The expectation that real benefits in technology will arise from ionic liquid research and the development of new processes is high, but there is a need for further work to demonstrate the credibility of ionic liquid-based processes as viable green technology. In particular, comprehensive toxicity studies, physical and chemical property collation and dissemination, and realistic comparisons to traditional systems are needed. It is clear that while the new chemistry being developed in ionic liquids is exciting, many are losing sight of the green goals and falling back on old habits in synthetic chemistry. Whereas it is true that incremental improvement is good, it is hoped that by focusing on a green agenda, new technologies can be developed that truly are not only better technologically, but are cleaner, cheaper, and safer as well."

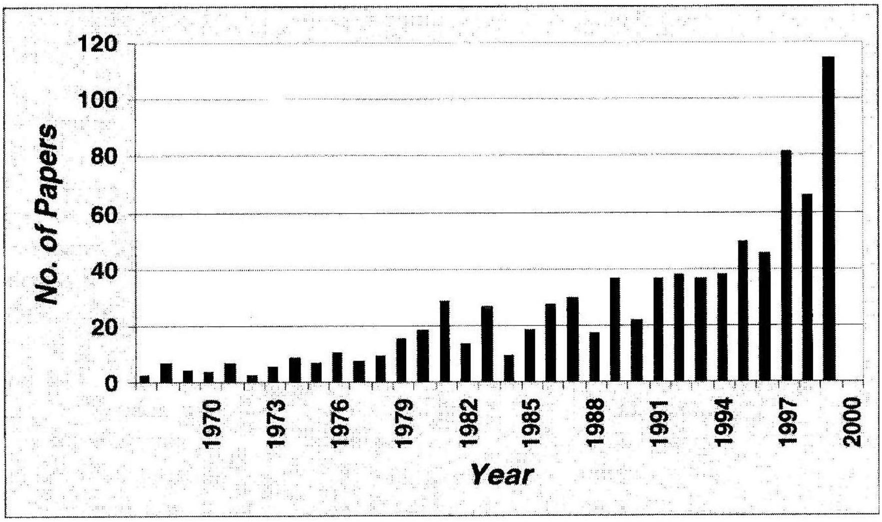

Figure 1: The rise in publications concerning ionic liquids as a function of time, as determined using SciFinder.

Robin's response is insightful. It reflects, in part, the burgeoning growth of papers in this area (see Figure 1) combined with the inevitable (and welcomed) rise in new researchers entering the area. However, with increasing activity comes the inevitable increasing "garbage" factor. In recent years we have (unfortunately) seen papers reporting physical data on ionic liquids that were demonstrably impure, liquids reported as solids and solids reported as liquids because of the impurity level, communications "rediscovering" and publishing work (without citation) already published in the patent literature, the synthesis of water-sensitive ionic liquids under conditions that inevitably result in hydrolysis, and academically weak publications appearing in commercial journals with lax refereeing standards. I truly believe that this book will help combat this; it should, and will, be referred to by all workers in the field. Indeed, if the authors citing it actually read it too, then the garbage factor should become insignificantly small!

In conclusion, this volume reflects well the excitement and rapid progress in the field of ionic liquids, whilst effectively providing an invaluable hands-on instruction manual. The lacunae are emphasised, and the directions for potential future research are clearly signposted. Unlike Snow in his renowned *Two Cultures* essay, many of us (Mamantov, Osteryoung, Wilkes, and Hussey, to name but a few of the founding fathers) who entered this area in its early (but not earliest!!) days prided ourselves that the science we were doing could not fail to have a practical use. Whether that use was battery applications, fuel cells, electroplating, nuclear reprocessing, or green industrial synthesis, we all believed that ionic liquids (or room-temperature molten salts, as they were then commonly known) offered a unique chemical environment that would (*must*) have significant industrial application. Because of this, we suffered then (and to some extent now) from the disdain of the "pure" scientists, who failed (and still fail) to appreciate that, if selecting an example to study to illustrate a fundamental scientific principle, there is actually some merit in selecting a product manufactured at the one million ton per annum level, rather than an esoteric molecule of no use and even less interest. Unfortunately, the pride and superiority Snow refers to is still alive and well, and living in the hearts of some of the academic establishment. I believe that this book will help tackle this prejudice, and illustrate that useful practical applications and groundbreaking fundamental science are not different, opposing areas, but synergistic sides of the same coin.

K.R. Seddon
May, 2002

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. The book is intended to be didactic, with examples from the literature used to illustrate and explain. Therefore, not all chapters will give a comprehensive coverage of the literature in the area. Indeed, with the explosion of interest in some applications of ionic liquids comprehensive coverage of the literature would not be possible in a book of this length. Finally, there is a point when one has to stop and for us that was the end of 2001. We hope that no offence is caused to anyone whose work has not been included. None is intended.

Acknowledgements

We would like to sincerely thank everyone who has been involved in the publication of this book. All of 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. When embarking on this project we were both regaled with stories of books that never saw the light of day because of missed deadlines and the general tardiness of contributors. All of our colleagues have met their commitments in the most timely and enthusiastic manner. 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. Karen Kriese.

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 apologise unreservedly for any mistakes that have found their way into the book.

P. Wasserscheid, T. Welton
August, 2002

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Contents

1
Introduction

John S. Wilkes

Ionic liquids may be viewed as a new and remarkable class of solvents, or as a type of materials that have a long and useful history. In fact, ionic liquids are both, depending on your point of view. It is absolutely clear though, 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 had grown to over 300 in 2001. The increased interest is clearly due to the realization that these materials, formerly used for specialized electrochemical applications, may have greater utility as reaction solvents.

For 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 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, except perhaps some liquid polymers, can match the liquidus range of ionic liquids or molten salts. Ionic liquids differ from molten salts in just where the liquidus range is in the scale of temperature.

There are many synonyms used for ionic liquids, which can 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 niche 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