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ELECTROCHEMICAL ASPECTS of IONIC LIQUIDS

Edited by HIROYUKI OHNO

Electrochemical Aspects of Ionic Liquids

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WILEY-INTERSCIENCE

A JOHN WILEY & SONS, INC., PUBLICATION

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

Library of Congress Cataloging-in-Publication Data:

Electrochemical aspects of ionic liquids / edited by Hiroyuki Ohno.
p. cm.
Includes bibliographical references.
ISBN 0-471-64851-5 (cloth)
1. Ionic solutions. 2. Electrochemistry. 3. Polymerization.
I. Ohno, Hiroyuki, 1953-II. Title.

QD562.165E38 2005
541′.372–dc22 2004019936

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

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Preface

This book introduces some basic and advanced studies on ionic liquids in the electrochemical field. Although ionic liquids are known by only a few scientists and engineers, their applications' potential in future technologies is unlimited. There are already many reports of basic and applied studies of ionic liquids as reaction solvents, but the reaction solvent is not the only brilliant future of the ionic liquids. Electrochemistry has become a big field covering several key ideas such as energy, environment, nanotechnology, and analysis. It is hoped that the contributions on ionic liquids in this book will open other areas of study as well as to inspire future aspects in the electrochemical field. The applications of ionic liquids in this book have been narrowed to the latest results of electrochemistry. For this reason only the results on room-temperature ionic liquids are presented, and not on high-temperature melts.

The reader of this book should have some basic knowledge of electrochemistry. Those who are engaged in work or study of electrochemistry will get to know the great advantages of using ionic liquids. Some readers may find the functionally designed ionic liquids to be helpful in developing novel materials not only in electrochemistry but also in other scientific fields. This book covers a wide range of subjects involving electrochemistry. Subjects such as the solubilization of biomolecules may not seem to be necessary for electrochemistry concerning ionic liquids, but some readers will recognize the significance of solubility control of functional molecules in ionic liquids even in an electrochemical field. Many more examples and topics on ionic liquids as solvents have been summarized and published elsewhere, and the interested reader will benefit from studying the references that are provided at the end of each chapter.

Acknowledgments

To prepare this book, many authors who are at the cutting edge of their areas of study have kindly agreed to write these chapters. This book should enable a practicing scientists to develop their own original research.

I would like to express my sincere thanks to all these authors. They were all very cooperative and summarized their progress despite their very busy schedules. This book therefore shares the fruits of their highly original, individual work.

I would also like to acknowledge Prof. Dr. K. R. Seddon of Queen's University of Belfast, England. He strongly urged me to publish this book when he saw the table of contents written in English. During his stay at our laboratory in January 2003, I explained to him the concept and the strong points of such a book. Without his urging, this book would not have been published.

I would like to extend my appreciation to all members of our laboratory in the Department of Biotechnology, Tokyo University of Agriculture and Technology. Especially Dr. M. Yoshizawa receives my most sincere thanks. This book would not have been finished without his sacrifices. Last I would like to thank Dr. Arza Seidel of John Wiley and Sons, Inc. for her kind support and encouragement.

HIROYUKI OHNO

Contents

Chapter 1

Importance and Possibility of Ionic Liquids

Hiroyuki Ohno

1.1 IONIC LIQUIDS

Ionic liquids are the salts having very low melting temperature. Ionic liquids have received great interests recently because of their unusual properties as liquids. These unique properties of ionic liquids have already been mentioned in some books, so we do not repeat them here more than simply summarize them in Table 1.1. Note these are entirely different properties from those of ordinary molecular liquids. The most important properties of electrolyte solutions are nonvolatility and high ion conductivity. These are essentially the properties of advanced (and safe) electrolyte solutions that are critical to energy devices put in outdoor use. Safety is more an issue than performance these days, and is taken into account in the trends in the materials developed for practical. Thus more developments in ionic liquids are expected to be seen in the future. The nonvolatile electrolyte solution will change the performance of electronic and ionic devices. These devices will become safer and have longer operational lives. But, more interesting, they will be composed of organic ions, and these organic compounds will have unlimited structural variations because of the easy preparation of many components. So there are unlimited possibilities open to the new field of ionic liquids. The most compelling idea is that ionic liquids are "designable" or "fine-tunable." So we can easily expect explosive developments in fields using these remarkable materials.

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ISBN 0-471-64851-5

TABLE 1.1 Basic Characteristics of Organic Ionic Liquids

Low melting point	• Treated as liquid at ambient temperature • Wide usable temperature range
Non-volatility	• Thermal stability • Nonflammability
Composed by Ions	• High ion density • High ion conductivity
Organic ions	• Various kinds of salts • Designable • Unlimited combination

1.2 IMPORTANCE OF IONIC LIQUIDS

Ionic liquids are salts that melt at ambient temperature. The principles of physical chemistry involved in the great difference between solution properties of molecular solvents and molten salts have already been introduced and summarized in a number of books. Thousands of papers have already been published on their outstanding characteristics and effectiveness for a variety of fields. Thus, as was mentioned above, in this book we take the most important point that these ionic salts are composed of organic ions and explore the unlimited possibility of creating extraordinary materials using molten salts.

Because ionic liquids are composed of only ions, they show very high ionic conductivity, nonvolatility, and nonflammability. The nonflammable liquids with high ionic conductivity are practical materials for use in electrochemistry. At the same time the nonflammability and nonvolatility inherent in ion conductive liquids open new possibilities in other fields as well. Because most energy devices can accidentally explode or ignite, for motor vehicles there is plenty of incentive to seek safe materials. Ionic liquids are being developed for energy devices. It is therefore important to have an understanding of the basic properties of these interesting materials. The ionic liquids are multi-purpose materials, so there should be considerable (and unexpected) applications. In this book we, however, will not venture into too many other areas. Our concern will be to assess the possible uses of ionic liquids in electrochemistry and allied research areas.

1.3 POTENTIAL OF IONIC LIQUIDS

At present most of the interest in ionic liquids is centered on the design of new solvents. While the development of "new solvents" has led the direction of possible applications for ionic liquids, there is more potential for development electrochemical applications.

Electrochemistry basically needs two materials: electro conductive materials and ion conductive materials. Ionic liquids open the possibility of improving ion conductive materials. The aqueous salt solution is one of the best electrolyte solutions

for electrochemical studies. However, because water is volatile, it is impossible to use this at wide temperature range or on a very small scale. Many other organic polar solvents have been used instead of water to prepare electrolyte solutions. They, however, have more or less the same drawback, depending on the characteristics. The material known to be a nonvolatile ion conductor is the polymer electrolyte. Polymers do not vaporize but decompose at higher temperatures; the vapor pressure at ambient temperature is zero. Polymer electrolytes are considered a top class of electrolytes except for the one drawback: relatively low ionic conductivity.

Some of the literature has included statements that the ionic liquids are thermally stable and never decompose. This kind of statement has led to a misunderstanding that the ionic liquids are never vaporized and are stable even when on fire. Are the ionic liquids indestructable? The answer is no. However, while inorganic salts are entirely stable, the thermal stability of organic salts depends largely on their structure. Since most recently reported ionic liquids are organic compounds, their degradation begins at the weakest covalent bond. Nevertheless, ionic liquids are stable enough for ordinary use at temperatures of 200° to 300°C. So it is not difficult to design novel ionic liquids that can be decomposed at certain temperature or by certain trigger. It is also possible to design unique catalysts (or catalytic systems) that can decompose target ionic liquids. Some catalysts such as metal oxides or metal complexes have the potential to become excellent catalysts for the decomposition of certain ionic liquids under mild conditions. The post-treatment technologies of ionic liquids should therefore also be developed along with the work on the design of ionic liquids.

At the present time there has been little progress in this area. Although post-treatment technologies are beyond the scope of this book, we do attempt to give ideas on the various future developments in ionic liquid technologies as well as in electrochemistry. This book is dedicated to introducing, analyzing, and discussing ionic liquids as nonvolatile and highly ion conductive electrolyte solutions. The astute reader will find the future prospects for ionic liquids between the lines in all chapters of this book.

Chapter 2

Physical Chemistry of Ionic Liquids, Inorganic and Organic, Protic and Aprotic

C. A. Angell, W. Xu, M. Yoshizawa, A. Hayashi,
J.-P. Belieres, P. Lucas, and M. Videa

2.1 CLASSES OF IONIC LIQUIDS

Ionic liquids in their high temperature manifestations (liquid oxides, silicates, salts) have been studied for a long time, using quite sophisticated methods, and much of the physics is understood. By contrast, the low temperature ionic liquid field, the subject of the present volume, is very much in its formative stages. The many studies on the interesting transport properties of ionic liquids and thermodynamic properties have focused mainly on characterizing new systems for potential applications [1–5]. The job of placing ion conductive behavior within the wider phenomenology of liquid and amorphous solid electrolytes, and of the liquid state in general, has barely begun. In this chapter we review the collective physical properties of ionic liquids in an attempt to place them within this larger picture.

The first requirement of an ionic liquid is that, contrary to experience with most liquids consisting of ions, it must have a melting point that is not much above room temperature. The limit commonly suggested is 100°C [1b]. Given the cohesive energy of ionic liquids (about which more will be said below), ambient melting requires that the melting point occur at a temperature not too far above the glass

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