ELECTROCHEMICAL ASPECTS OF IONIC LIQUIDS

Second Edition

Edited by

HIROYUKI OHNO

WILEY
A JOHN WILEY & SONS, INC., PUBLICATION
ELECTROCHEMICAL
ASPECTS OF IONIC
LIQUIDS
ELECTROCHEMICAL ASPECTS OF IONIC LIQUIDS

Second Edition

Edited by

HIROYUKI OHNO

WILEY
A JOHN WILEY & SONS, INC., PUBLICATION
CONTENTS

PREFACE TO THE SECOND EDITION ix
PREFACE TO THE FIRST EDITION xi
ACKNOWLEDGMENTS FOR THE SECOND EDITION xiii
CONTRIBUTORS xv

1 Importance and Possibility of Ionic Liquids 1
   Hiroyuki Ohno

2 Physical Chemistry of Ionic Liquids: Inorganic and Organic as Well as Protic and Aprotic 5

PART I    BASIC ELECTROCHEMISTRY 33

3 General Techniques 35
   Yasushi Katayama

4 Electrochemical Windows of Room-Temperature Ionic Liquids (RTILs) 43
   Hajime Matsumoto
CONTENTS

5 Diffusion in Ionic Liquids and Correlation with Ionic Transport Behavior 65
Md. Abu Bin Hasan Susan, Akihiro Noda, and Masayoshi Watanabe

6 Ionic Conductivity 87
Hiroyuki Ohno, Masahiro Yoshizawa-Fujita, and Tomonobu Mizumo

7 Optical Waveguide Spectroscopy 95
Hiroyuki Ohno and Kyoko Fujita

8 Electrolytic Reactions 101
Toshio Fuchigami and Shinsuke Inagi

9 Electrodeposition of Metals in Ionic Liquids 129
Yasushi Katayama

PART II BIOELECTROCHEMISTRY 157

10 Enzymatic Reactions 159
Noritaka Iwai and Tomoya Kitazume

11 Molecular Self-assembly in Ionic Liquids 169
Nobuo Kimizuka and Takuya Nakashima

12 Solubilization of Biomaterials into Ionic Liquids 183
Kyoko Fujita, Yukinobu Fukaya, and Hiroyuki Ohno

13 Redox Reaction of Proteins 193
Kyoko Fujita and Hiroyuki Ohno

PART III IONIC DEVICES 203

14 Li Batteries 205
Hikari Sakaebé and Hajime Matsumoto

15 Photoelectrochemical Cells 221
Hajime Matsumoto

16 Fuel Cells 235
Masahiro Yoshizawa-Fujita and Hiroyuki Ohno

17 Double-Layer Capacitors 243
Makoto Ue
<table>
<thead>
<tr>
<th>CONTENTS</th>
<th>v</th>
</tr>
</thead>
<tbody>
<tr>
<td>18 Actuators 271</td>
<td>Kinji Asaka</td>
</tr>
<tr>
<td><strong>PART IV FUNCTIONAL DESIGN</strong></td>
<td>279</td>
</tr>
<tr>
<td>19 Novel Fluoroanion Salts 281</td>
<td>Rika Hagiwara and Kazuhiko Matsumoto</td>
</tr>
<tr>
<td>20 Neutralized Amines 293</td>
<td>Hiroyuki Ohno</td>
</tr>
<tr>
<td>21 Zwitterionic Liquids 301</td>
<td>Masahiro Yoshizawa-Fujita, Asako Narita, and Hiroyuki Ohno</td>
</tr>
<tr>
<td>22 Alkali Metal Ionic Liquids 317</td>
<td>Wataru Oghara, Masahiro Yoshizawa-Fujita, and Hiroyuki Ohno</td>
</tr>
<tr>
<td>23 Polyether/Salt Hybrids 325</td>
<td>Tomonobu Mizumo and Hiroyuki Ohno</td>
</tr>
<tr>
<td>24 Electric Conductivity and Magnetic Ionic Liquids 337</td>
<td>Gunzi Saito</td>
</tr>
<tr>
<td><strong>PART V IONIC LIQUIDS IN ORDERED STRUCTURES</strong></td>
<td>347</td>
</tr>
<tr>
<td>25 Ion Conduction in Organic Ionic Plastic Crystals 349</td>
<td>Maria Forsyth, Jennifer M. Pringle, and Douglas R. MacFarlane</td>
</tr>
<tr>
<td>26 Liquid Crystalline Ionic Liquids 375</td>
<td>Takashi Kato and Masafumi Yoshio</td>
</tr>
<tr>
<td><strong>PART VI GEL-TYPE POL YMER ELECTROLYTES</strong></td>
<td>393</td>
</tr>
<tr>
<td>27 Ionic Liquid Gels 395</td>
<td>Kenji Hanabusa</td>
</tr>
<tr>
<td>28 Zwitterionic Liquid/Polymer Gels 403</td>
<td>Masahiro Yoshizawa-Fujita and Hiroyuki Ohno</td>
</tr>
<tr>
<td>29 Ionic Liquidized DNA 409</td>
<td>Naomi Nishimura and Hiroyuki Ohno</td>
</tr>
</tbody>
</table>
PART VII  POLYMERIZED IONIC LIQUIDS 417

30  Ion Conductive Polymers 419
   Hiroyuki Ohno and Masahiro Yoshizawa-Fujita

31  Amphoteric Polymers 433
   Hiroyuki Ohno, Masahiro Yoshizawa-Fujita, and Wataru Oghara

32  Polymer Brushes 441
   Masahiro Yoshizawa-Fujita and Hiroyuki Ohno

PART VIII  CONCLUSION 457

33  Future Prospects 459
   Hiroyuki Ohno

APPENDIX: STRUCTURES OF ZWITTERIONS 463

INDEX 465
The first edition of this book was published in 2005 as the first book on the basic study and application of the ionic liquids for electrochemical aspects. At this time, there is increasing interest in ionic liquids as an electrolyte solution substituent. In particular, interests are focused on the safety of the organic ion conductive liquids. Despite the safety of ionic liquids, there is still hesitation in using these ionic liquids as an electrolyte solution. This might be caused by two major reasons, one is cost, and the other is the great possibility of the development of better ionic liquids. The former is actually important for industry, but it should also be a matter of demand. Larger demand lowers the price. The second reason is a bit serious, because there is always the possibility of finding or developing new and better ionic liquids. There should be a kind of hesitation in deciding on the industrial use of current ionic liquids, because no one can deny that there is the possibility that better ones will emerge. In any case, it should be most important to develop ionic liquids having sufficient properties for practical use. Understanding of the latest in ionic liquid science is important to provide motivation for researchers to use them.

In the second edition, we considerably updated the content to catch up with the fast changes in ionic liquid science. Also, interesting new chapters have been added. In every chapter, we tried to add the latest information while keeping the number of pages as low as possible. It will be one of our great pleasures if readers find some interesting point regarding ionic liquid science that aids in their research.

HIROYUKI OHNO
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.

HIROYUKI OHNO

xi
ACKNOWLEDGMENTS FOR THE SECOND EDITION

First of all, I would like to express my sincere thanks to all the contributors for the second edition. All authors kindly agreed to reuse their chapters and made an effort to put the latest information in every chapter. A new chapter has been added in the second edition for better reviewing in electrochemistry.

Next an acknowledgment should be given to Dr. Naomi Nishimura of the Department of Biotechnology, Tokyo University of Agriculture and Technology. Naomi worked hard to help me to edit manuscripts. She was so systematic that there were no serious problems in the editing of the manuscript. Without her energetic contribution, this book would not be published by the due date.

Finally I would like to thank Dr. Arza Seidel of John Wiley and Sons, Inc. for her kind support and encouragement.

HIROYUKI OHNO
CONTRIBUTORS

C. Austen Angell, Department of Chemistry and Biochemistry, Arizona State University

Younes Ansari, Department of Chemistry and Biochemistry, Arizona State University

Kinji Asaka, National Institute of Advanced Industrial Science and Technology (AIST)

Jean-Philippe Belieres, Department of Chemistry and Biochemistry, Arizona State University

Maria Forsyth, Department of Materials Engineering, Monash University

Toshio Fuchigami, Department of Electronic Chemistry, Tokyo Institute of Technology

Kyoko Fujita, Department of Biotechnology, Tokyo University of Agriculture and Technology

Masahiro Yoshizawa-Fujita, Department of Materials and Life Sciences, Sophia University

Yukinobu Fukaya, Department of Biotechnology, Tokyo University of Agriculture and Technology

Dominic Gervasio, Center for Applied Nanobioscience in the BioDesign Institute and School of Materials, Arizona State University

Rika Hagiwara, Department of Fundamental Energy Science, Kyoto University
CONTRIBUTORS

Kenji Hanabusa, Graduate School of Science and Technology, Shinshu University

Akitoshi Hayashi, Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University

Shinsuke Inagi, Department of Electronic Chemistry, Tokyo Institute of Technology

Noritaka Iwai, Department of Bioengineering, Tokyo Institute of Technology

Yasushi Katayama, Department of Applied Chemistry, Faculty of Science and Technology, Keio University

Takashi Kato, Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo

Nobuo Kimizuka, Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University

Tomoya Kitazume, Department of Bioengineering, Tokyo Institute of Technology

Pierre Lucas, Department of Chemistry and Biochemistry, Arizona State University

Douglas R. MacFarlane, School of Chemistry, Monash University

Hajime Matsumoto, Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST)

Kazuhiko Matsumoto, Graduate School of Energy Science, Kyoto University

Tomonobu Mizuno, Department of Applied Chemistry, Hiroshima University

Takuya Nakashima, Graduate School of Materials Science, Nara Institute of Science and Technology

Asako Narita, Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University

Naomi Nishimura, Department of Biotechnology, Tokyo University of Agriculture and Technology

Akihiro Noda, Honda R & D Co., Ltd.

Wataru Ogihara, Nissan Motor Co., Ltd.

Hiroyuki Ohno, Department of Biotechnology, Tokyo University of Agriculture and Technology

Jennifer M. Pringle, Department of Materials Engineering and School of Chemistry, Monash University

Gunzi Saito, Research Institute, Meijo University
CONTRIBUTORS

Hikari Sakaibe, Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST)

Md. Abu Bin Hasan Susan, Department of Chemistry, University of Dhaka

Jeffery Thomson, Center for Applied Nanobioscience in the BioDesign Institute and School of Materials, Arizona State University

Makoto Ue, Fellow, Mitsubishi Chemical Corporation

Kazuhide Ueno, Department of Chemistry and Biochemistry, Arizona State University

Marcelo Videa, Department of Chemistry and Biochemistry, Arizona State University

Masayoshi Watanabe, Department of Chemistry and Biotechnology, Yokohama National University

Xu Wu, Department of Chemistry and Biochemistry, Arizona State University

Masafumi Yoshio, Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo

Zuofeng Zhao, Department of Chemistry and Biochemistry, Arizona State University
1

IMPORTANCE AND POSSIBILITY OF IONIC LIQUIDS

HIROYUKI OHNO

1.1 IONIC LIQUIDS

Ionic liquids are salts with a very low melting temperature. Ionic liquids have been of great interest recently because of their unusual properties as liquids. Because these unique properties of ionic liquids have been mentioned in a few other books, we will not repeat them here but will summarize them in Table 1.1. Note that these are entirely different properties from those of ordinary molecular liquids. Also, every ionic liquid does not always show these properties. For electrochemical usage, the most important properties should be both 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 a more important issue than performance these days, and it has been taken into account in the materials developed for practical use. Thus, more developments in ionic liquids are expected in the future. The nonvolatile electrolyte solution will change the shape and performance of electronic and ionic devices. These devices will become safer and have longer operational lives. They are composed of organic ions, and these organic compounds have unlimited structural variations because of the easy preparation of many different 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.” Therefore, we can easily expect explosive developments in fields using these remarkable materials.

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 several books. Thousands of papers have already been published on their outstanding characteristics and effectiveness for a variety of fields. Thus, as mentioned, in this book, we take the most important point that these 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 usually show very high ionic conductivity, nonvolatility, and flame retardancy. The organic liquids with both high ionic conductivity and flame retardancy are practical materials for use in electrochemistry. At the same time, the flame retardancy based on nonvolatility inherent in ion conductive liquids opens 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 multipurpose 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 interest in ionic liquids is centered on the design of new solvents. Although the development of “new solvents” has led the development of possible applications for ionic liquids, there is more potential for development of electrochemical applications.

Electrochemistry basically needs two materials: electroconductive materials and ion conductive materials. Ionic liquids open the possibility of improving

---

**TABLE 1.1. Basic and Possible Characteristics of Organic Ionic Liquids**

<table>
<thead>
<tr>
<th>Feature</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low melting point</td>
<td>Treated as liquid at ambient temperature</td>
</tr>
<tr>
<td></td>
<td>Wide usable temperature range</td>
</tr>
<tr>
<td>Nonvolatility</td>
<td>Thermal stability</td>
</tr>
<tr>
<td></td>
<td>Flame retardancy</td>
</tr>
<tr>
<td>Composed by ions</td>
<td>High ion density</td>
</tr>
<tr>
<td></td>
<td>High ion conductivity</td>
</tr>
<tr>
<td>Organic ions</td>
<td>Various kinds of salts</td>
</tr>
<tr>
<td></td>
<td>Designable</td>
</tr>
<tr>
<td></td>
<td>Unlimited combinations</td>
</tr>
</tbody>
</table>
POTENTIAL OF IONIC LIQUIDS

ion conductive materials. The aqueous salt solution is one of the best electro-
lyte solutions for electrochemical studies. However, because water is volatile,
it is impossible to use this at a 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.

One remarkable property of ionic liquids is the proton conduction at a
temperature higher than 100 °C. Water-based proton conductors cannot be
operated at such a high temperature because of vaporization of water. As
mentioned in a later chapter, proton-conductive ionic liquids are the most
expected materials.

Some literature has included statements that the ionic liquids are thermally
stable and never decompose. This kind of statement has led to a misunder-
standing that the ionic liquids are never vaporized and are stable even when
on fire. Are the ionic liquids indestructible? The answer is “no.” However,
although inorganic salts are entirely stable, the thermal stability of organic
salts depends largely on their structure. Because ionic liquids are organic
compounds, their degradation begins at the weakest covalent bond by heating.
Nevertheless, ionic liquids are stable enough at temperatures of 200 °C to
300 °C. This upper limit is high enough for ordinary use.

Does it need more energy or cost to decompose ionic liquids after finis-
ishing their role? It is not difficult to design novel ionic liquids that can be decom-
posed at a certain temperature or by a certain trigger. It also is 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 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 electro-
lyte solutions. The astute reader will find the future prospects for ionic liquids
between the lines in all chapters of this book.
2

PHYSICAL CHEMISTRY OF IONIC LIQUIDS: INORGANIC AND ORGANIC AS WELL AS PROTIC AND APROTIC


2.1 CLASSES OF IONIC LIQUIDS

Ionic liquids in their high-temperature manifestations (liquid oxides, silicates, and salts) have been studied for a long time, using sophisticated methods, and much of the physics is understood. By contrast, the low-temperature ionic liquid (IL) field (<100 °C ILs), the subject of the present volume, is still under development. The many interesting studies on transport and thermodynamic properties of the <100 °C ILs have focused mainly on characterizing new systems for potential applications [1–5]. The task of placing this behavior within the wider phenomenology of liquid and amorphous solid electrolytes as well as in the context of the liquid state in general still has a long way to go. In this chapter, we review the current state of knowledge of physical properties of ionic liquids in an attempt to place them within this larger picture. We make an effort to emphasize the special status of the protic subclass of ionic liquids because these offer a degree of freedom not encountered in other branches of the solvent-free liquid state.

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...
higher than room temperature. The limit commonly suggested is \(100^\circ\text{C}\)\[^{1b}\]. Given the cohesive energy of ionic liquids (about which more will be said later on), ambient melting requires that the melting point occur at a temperature not too much higher than the glass transition temperature, \(T_g\), which provides the natural base for liquid-like behavior. Ionic liquids nearly all melt within the range that we call the “low-temperature regime” of liquid behavior \[^{6,7}\]. This means that in most cases, they will supercool readily and will exhibit “super-Arrhenius” transport behavior near and below ambient temperature—as is nearly always reported.

Such liquids come in different classes. The most heavily researched class is the aprotic organic cation class \[^{1–4,8–15}\]. In this cation class, the low melting point is a consequence of the problem of efficiently packing large, irregular organic cations with small inorganic anions. More on this class is given in Section 2.3.

A second class \[^{16}\] is one that may enjoy increased interest in the future because of the presence of one of its members in the first industrial IL process \[^{1b}\], because of the new finding that its members can have aqueous solution-like conductivities \[^{17}\] and can serve as novel electrolytes for fuel cells \[^{18}\], and finally, because of the evidence that these liquids, in hydrated form, can be used as tunable solvents for biomolecules, on which stability against aggregation and hydrolysis may be provided under the right tuning \[^{19}\]. This class is closely related to the first but differs in that the cation has been formed by transfer of a proton from a Brønsted acid to a Brønsted base. The process is reversible if the free energy of proton transfer is not too large. When the gap across which the proton must jump to reform the original molecular liquid is small, the liquid will have a low conductivity and a high vapor pressure. These properties are not of great interest in an ionic liquid, although the liquid may be fluid. If the gap is large, as in the case of ammonium nitrate, \(87\,\text{kJ/mol}\) (from data for \(\text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4\text{NO}_3\)), then the proton will remain largely on the cation, and for many purposes, the system is a molten salt. If the acid is a strong acid like triflic acid, \(\text{HSO}_3\text{CF}_3\), or a superacid like HTFSI \[^{16}\], then the transfer of the proton will be energetic, and the original acid will not be regenerated on heating before the organic cation decomposes. Such liquids will not be easily distinguishable in properties from the conventional aprotic salts in which some alkyl group, rather than a proton, has been transferred to the basic site. This is particularly true of the protic ionic liquids (PILs) recently reported by Luo et al. \[^{20}\] using superbases as proton acceptors. The stability of these systems has been characterized in terms of the relation between the boiling point elevation (or excess boiling point) over the linear (or average value) of the components \[^{21}\], and the excess was shown to be a linear function of the difference in \(pK_a\) values determined in aqueous solutions.

This relation is shown in Figure 2.1. It seems to be free of exceptions when the base is a simple amine nitrogen. The protic ionic liquids as a class \[^{16–18}\] are considerably more fluid than the aprotic ionic liquids \[^{17}\], most likely because of their generally reduced ionicity (see Section 2.6).
The third and distinct class of ionic liquid is the one that consists entirely of inorganic entities. These are formed mostly as a consequence of the mismatch of large anions like tetrachloroaluminate or iodide with small cations like Li$^+$. The eutectic in the system LiAlCl$_4$–LiAlI$_4$ system, for instance, lies at 65 °C, and the liquid is highly fluid—more fluid than most aprotic ionic liquids. The phase diagram is shown in Figure 2.2 [22]. Also in this group is the more viscous system containing silver and alkali halides [23], which exhibits an ambient temperature electrical conductivity, 10$^{-14}$ S/cm, that is higher than that of any aprotic ionic liquid because of the highly decoupled state of the silver ions. Here, a protic subclass also may be important; in fact the first “ionic liquids” made were probably of this type, namely mixtures of ammonium salts like the NH$_4$SCN and NH$_4$NO$_3$ eutectic recently shown to provide interesting...
fuel cell electrolytes [24]. Hydrazinium nitrate is known to melt at 80°C [25]. Waiting to be created here is a subclass in which the cations are derived from inorganic molecular entities, for instance, \( (\text{PNCI}_2)_3 \) or \( (\text{SN})_4 \). A protic salt of the latter is on record, but its melting point is unknown. We have obtained a sharply melting compound \( (\text{PNCI}_2)_3 \cdot \text{HTFSI} \), from the equimolar melt of the components [26], but its conductivity is too low to class it as an ionic liquid (i.e., it is of low “ionicity” [27–31]). The nitrogen atoms of \( \text{PNCI}_2 \) are known to be only weakly basic, so the salt, if formed with a stronger acid (e.g., \( \text{HSbF}_6 \)), although of higher ionicity, also would be of high “acidity” [32]; in fact, it would be a member of the class of superacidic ionic liquids [33] that we will describe subsequently.

A fourth class may be considered, although it contains nonionic entities. This is the liquid state of various ionic solvates. In these systems, molecules usually thought of as solvent molecules are bound tightly to high field cations and have no solvent function. Such “molten solvates” have low vapor pressures at ambient temperatures and only boil at temperatures near 200°C; for instance, \( \text{LiZnBr}_4 \cdot 3\text{H}_2\text{O} \), has \( T_b = 190 °\text{C} \), whereas \( T_g = -120 °\text{C} \) [34].

To provide a better perspective on ionic liquids, we first make some observations on inorganic salts and the factors that make it possible to observe them as ionic liquids below 100°C.
2.2 LOW-TEMPERATURE LIQUID BEHAVIOR OF IONIC MELTS

Most inorganic salts, when they melt, are found to flow and conduct electricity according to a simple Arrhenius law at all temperatures down to their melting points. For instance, unless measurements of high precision are used, the alkali halides seem to obey the Arrhenius equation, even down to the deep eutectic temperatures of their mixtures with other salts. LiCl and KCl form a eutectic mixture with a freezing point of 351 °C, approximately 300 K below either pure salt freezing point; yet the viscosity of the melt barely departs from Arrhenius behavior before freezing.

To see the viscosity behavior of the highly super-Arrhenius type typical of almost any individual room-temperature molten salt (RTMS), it is necessary to avoid alkali halides altogether and examine salts that cannot form such symmetrical crystal lattices. For instance, alkali nitrates, like KNO₃, do not occupy much more volume in the liquid state than KI, but they melt at much lower temperatures. However, even KNO₃ exhibits an Arrhenius-type viscosity temperature dependence according to any but the most precise measurements. It is only with deep eutectics like those for the ternary systems LiNO₃–NaNO₃–KNO₃ ($T_E = 143$ °C) and LiNO₃–NaNO₂–KNO₃ ($T_E = 125$ °C) that one starts to observe clear deviations from the Arrhenius law [6a,7]. This stands in clear contrast with the behavior of the ILs (RTMS) or molten hydrates.

With all <100 °C ILs, deviations from the Arrhenius law, considerably in excess of those noted for the ternary LiNaK nitrate eutectic, are found well above their melting points. There is no need, with such ILs, to invoke eutectic mixtures to extend the stable liquid range to observe the “low-temperature domain” behavior. The low-temperature domain typically is found in the temperature range at $T < 2T_0$ [6], where $T_0$ is the theoretical low-temperature limit to the liquid state based on the Kauzmann extrapolation [35]. At $T_0$, extrapolations of experimental data suggest that the excess entropy of the liquid (excess over that of the crystal) would vanish and that the time scale for fluid flow would diverge [7,35]. The practical low-temperature limit to the liquid state given by the glass temperature, $T_g$, is considerably higher than the theoretical $T_0$, by an amount that depends on the liquid fragility. Typically $T_g/T_0 = 1.2–1.3$, unless the liquid is “strong” [35b]. So the low-temperature domain is entered at $T_g/T = 0.53–0.66$. For Arrhenius behavior, which represents the “strong” liquid limit of behavior is rarely observed, $T_0 = OK$ and $T_g/T_0 = \infty$. The upper end of this range, $T_g/T = 0.66$, is the number usually associated with the ratio of $T_g/T_\alpha$, for glassformers (the “2/3 rule”), although we have argued elsewhere [36] that this is not a rule but a tautology.

The behavior of ionic liquids is familiar to workers experienced with molten hydrates. With molten hydrates, the cation size is increased effectively by the shell of water molecules shielding the central cation from its anionic neighbors such that the cation acquires a size not unlike those of cations in the typical IL. We show a selection of viscosity data for normal molten salts, molten
Figure 2.3. $T_g$-scaled Arrhenius plot showing data for molten salts ZnCl$_2$ and calcium potassium nitrate (CKN), with data for the calcium nitrate hydrate (Ca(NO$_3$)$_2$·8H$_2$O) and the tetrafluoroborates of quaternary ammonium (MOMNM$_E$E, M = methyl, E = ethyl) and 1-n-butyl-3-methyl-imidazolium (BMI) cations, and the bis-oxalatoborate (BOB) of the latter cation, in relation to other liquids of varying fragility (from Xu et al. [15]).

hydrates, and ionic liquids in Figure 2.2, using a scaled Arrhenius plot to bring a wide range of data together on a single plot. A blurred distinction between “normal” and “low-temperature” domain behavior can be made by putting a vertical line at about $T_g/T = 0.625$.

The deviations from Arrhenius behavior observed in the low-temperature regime of Figure 2.3 in most cases are well accounted for by the three-parameter Vogel–Fulcher–Tammann (VFT) equation [37] in the modified form:

$$\eta_0 = \eta_0 \exp\left(D/[T - T_0]\right)$$  \hspace{1cm} (2.1)

where $\eta_0$, $D$, and $T_0$ are constants, and $T_0$, the vanishing mobility temperature, lies below the glass transition temperature if a suitable range of data (>3 orders of magnitude) are included in the data fitting. The different curvatures in Figure 2.3 then are reproduced by variations in the parameter $D$ of equation (2.1) [6b].