

*IONIC
LIQUIDS*

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Foreword

As Chairmen of the Electrochemistry and Molten Salts Discussion Groups of the Chemical Society, it gave us great pleasure to welcome the conference Highly Concentrated Aqueous Solutions and Molten Salts, which our Groups cosponsored, at St. John's College, Oxford in July 1978.

During the meeting the editors of the present volume, and those giving lectures, came to the conclusion that the verbal presentations deserved to be expanded and to be more widely disseminated in a permanent form. Thus the articles which appear in this volume were commissioned and prepared.

A greater exchange of information between aqueous chemists and those concerned with molten salts is to be welcomed and to this end the present volume aims to focus attention on the borderline areas between the two in an attempt to facilitate a wider awareness of the concepts and methods appropriate to the respective specialities. Similarly, and particularly in the electrochemical field, a greater exchange of information between the academic and industrial practitioners of the subject is desirable.

The problems involved are not trivial but when the interactions in these largely (but not wholly) ionic liquids are better understood, this will surely be to the benefit of all concerned with solution chemistry.

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Preface

A number of recent events led to the appearance of this text at this particular time.

During 1978, the EUCHEM Conference on Molten Salts at Lysekil, Sweden, was closely followed by a meeting on Highly Concentrated Aqueous Solutions and Molten Salts in Oxford, jointly sponsored by the Electrochemistry Group and Molten Salts Discussion Group of the Chemical Society. The Second International Symposium on Molten Salts was held in Pittsburgh, U.S.A., later in the year as part of the Electrochemical Society's 154th meeting. The underlying reasons for this expanding interest and support of ionic liquids will become apparent.

Most of the chemical and biological processes of the natural world proceed in aqueous solutions. This factor clearly provided the scenario for the development of chemical sciences until the middle of this century, although it is worth recalling that Faraday verified his laws of electrolysis using molten lead chloride! To date, the structure of the ubiquitous liquid we know as water is still imperfectly understood in spite of a lifetime of study by, for example, Bernal. When a solute is introduced (especially when the resulting solutions are concentrated) many complicated processes and equilibria may arise, and these are considered in some of the ensuing chapters. The ordering that occurs in electrolyte solutions down to unimolar levels, observed in the Russian X-ray studies of the 1930s, may now be predicted by computer modeling; Stillinger at Bell Laboratories was one of the first to obtain the services of sufficiently large computers to carry out the necessary calculations. A number of chapters consider our latest understanding of the structure of electrolyte solutions and melts based on both experimental and simulation studies.

The extraction of aluminum from molten cryolite has become an established process over nearly a century of operation. However, the impact of new molten salt technologies really dawned only when uranium extraction became of military importance some forty years ago. In retrospect, the lack of enthusiasm for such simple ionic liquids as molten alkali halides for example, is astonishing, even if materials and handling aspects

do present unfamiliar difficulties. Nevertheless, applications in homogeneous nuclear reactors, fuel cells, refractory metal deposition, heat treatment, and metallizing are now being matched by theoretical advances. The quasilattice model for molten salts developed by Blander has recently been extended by Braunstein and Gal to highly concentrated aqueous solutions by incorporating water molecules into the coordination shell of the cation, and latterly the anion, sublattices. Čeleda, among others, has evolved an alternative quasilattice approach. Notwithstanding these advances, developments in aqueous solution and molten salt chemistry/electrochemistry have proceeded almost independently. We have recorded our concern about this situation in the past, but now at last we have a chance to do something positive by including chapters written by both molten salt and aqueous solution specialists. In many cases these authors are exploring the eschewed Mesopotamia of highly concentrated solutions through to dilute solutions of water in molten salts, discovering new links and unified treatments of solution theory, while pointing out the practical consequences of their deliberations. The experimental work in this area is extremely difficult, requiring controlled atmospheres of water vapor; meanwhile one is acutely aware that slightly damp and dirty melts may be behaving in less than predictable fashion.

By the very nature of this volume, its subject matter is rather diverse. Nevertheless, we hope that the themes of theory and application in *Ionic Liquids* will commend themselves to the reader.

Furthermore, we would like to point out that we have encouraged authors to give a selective and personal view rather than an encyclopedic treatment of their chosen topic. In this way they are free to emphasize those aspects of the field which they themselves consider to be of most pressing relevance. We trust that this will best stimulate new interest and awareness across the whole spectrum of solution concentrations.

What of the future? Molten salts in energy generation and storage appear to be attracting increasing attention. Applications extend across new storage batteries, fuel cells, heat transfer and storage, coal gasification, nuclear reactors, organic scrap pyrolysis, and materials recycling. Doubtless these, and many developments involving ionic liquids yet to come, owe much to the gradual realization that fossil fuel resources really are finite. Efficiency, recycling, and ecological soundness are at last being given the emphasis they deserve. The ever-tightening screws of scarcity and price promise to focus the minds, even of politicians and administrators, on the rewards of research and investment in these new technologies.

David G. Lovering
Douglas Inman

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