Preface

Over the past decade, ionic liquids (ILs) have received a considerable scientific attention due to their unique physical properties (such as low melting points, low vapor pressure, non-flammability, thermal and chemical stability, or broad electrochemical window) and wide range of potential applications. An appropriate combination of cations and anions makes them attractive as potential pharmaceutical ingredients, green solvents as well as, promising electrolytes for fuel cells and batteries. However, progress in electrochemical field is still hindered by the limited understanding of the charge transport mechanism as well as the interplay between molecular structure and dynamics in ionic conductors. Therefore, in the last years many efforts of scientific community have been dedicated to comprehend the behavior of electric conductivity in various ion-containing systems (protic, aprotic as well as polymerized ionic liquids) and under various thermodynamic conditions.

This book provides a comprehensive survey of electrical properties of ionic liquids and solids obtained from studies involving broadband dielectric spectroscopy (BDS) both at ambient and elevated pressure. The book begins by reviewing the synthesis, purification and characterization of ionic liquids, presented in Chap. 1. In the "*Introduction to Ionic Liquids*" selected physical properties of ionic liquids such as thermal stability, melting point, glass transition, semi-crystallinity and viscosity are also discussed.

In Chap. 2, with the ambitious title "*Rotational and translational diffusion in ionic liquids*", new insights into the dominant mechanisms of ionic conductivity and structural dynamics obtained from studies involving broadband dielectric spectroscopy (BDS), pulsed field gradient nuclear magnetic resonance, dynamic mechanical spectroscopy, and dynamic light scattering techniques are presented. Additionally, in the same section a novel approach to extract diffusion coefficients from dielectric spectra in an extra-ordinarily broad range spanning over 10 orders of magnitude is provided.

On the other hand, Chap. 3 discusses the molecular motions of room temperature ionic liquids (RTILs) in the timescale ranging from femto- to nanoseconds at ambient temperatures. Therein, we show that the interactions in RTILs are not only

governed by long-ranged Coulombic forces. Also hydrogen-bonding, pi–pi stacking and dispersion forces contribute significantly to the local potential energy landscape, making RTIL dynamics extremely complex.

Chapter 4 summarizes recent advances in high pressure dielectric studies of ionic liquids and solids. The pressure sensitivity of DC-conductivity is discussed in terms of activation volume parameter and dT_g/dP coefficient. Within this section the transport properties of ionic conductors are analyzed not only in T-P thermodynamic space but also as a function of volume. This procedure enable us to discuss the contributions of density and thermal effects to ion dynamics near T_g as well as to verify the validity of the thermodynamic scaling concept for ionic systems. We also address the role played by charge transport mechanism (vehicle vs. Grotthuss type) on the isobaric and isothermal dependences of DC-conductivity and conductivity relaxation times when approaching the glass transition.

Chapters 5 and 6 review recent efforts to investigate polymerized ionic liquids and polymer electrolytes, being respectively macromolecular counterparts of ILs and salts inserted into polymer matrix. Chapter 5 discusses the fundamental properties of polymerized ionic liquids such as molecular dynamics, charge transport and mesoscopic structure and compares them with the properties of monomers.

At the beginning of Chap. 6 we give a brief overview of the protocols usually employed to analysis the dielectric spectrum of polymer electrolytes. The quantitative change of dielectric relaxation in polymers with the addition of salts will then be discussed primarily based on results from polypropylene glycols. The focus of the last part of the chapter is placed on the relationship between ionic transport and polymer relaxation.

Chapter 7 describes the current level of understanding of the electrode | IL interface. We show that broadband impedance spectroscopy in a three-electrode setup yields electrode-potential-dependent double layer capacitance values of the electrode | IL interface. The results of dielectric studies are compared with information obtained from other techniques, such as scanning tunnelling microscopy, atomic force microscopy, surface force apparatus measurements, X-ray reflectivity measurements, surface-enhanced Raman spectroscopy and sum-frequency generation vibrational spectroscopy.

In Chap. 8 an overview on the recent results for electrochemical double layers in ionic liquids at flat, rough, and porous electrodes is given. We show that electrode polarization effects can be used to directly determine the complex dielectric function of ionic liquids at the interface with a metal electrode. Our approach allows thus a systematic investigation of the electric and dielectric properties of ionic liquids at metal interfaces and opens the perspectives of a better understanding of the physics of charge transport at solid interfaces.

The decoupling between structural and conductivity relaxation in various aprotic ionic liquids is reported in Chap. 9. Therein, we took advantage from several calorimetric techniques (e.g. AC-calorimetry, temperature modulated differential scanning calorimetry (TMDSC)) to probe the dynamic glass transition of ionic systems. We demonstrate that for ion conducting materials, a significant difference

between conductivity relaxation and shear relaxation (viscosity) can be found. Consequently, in some cases it is not an easy task to determine definitely the dynamic glass transition from dielectric relaxation data.

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