

INTRODUCTION

Thermal stabilities and phase behaviour of Ionic liquids is a point of interest for several researchers. In the book “Ionic Liquids: Theory, Properties, New Approaches”, (2011) Edited by Alexander Kokorin, (ISBN 978-953-307-349-1,) a detailed set of reviews on different aspects of Room Temperature Ionic Liquids [RTILs] is presented.

RTILs are entirely composed of ions, with extraordinary high ion density & high ionic conductivity. Hence they are also known as greener alternatives. Differential Scanning Calorimetry, Conductivity & Catalytic studies, interfacial impedance, Potentiometry, Cyclic Voltametry, E.M.F measurements, and other transport parameters, furnish bulk of data that forms the basis of chemical understanding of processes; while, Thermodynamic, Acoustic, Densimetric, Optical Fluorescence, Dielectric Relaxation, N.M.R. and Molecular Dynamic Simulation studies constitute the methods for the analysis of the ion- ion, Ion- solvent and solvent- solvent interactions which throw light on the involved Bio-chemical and Physio- Chemical mechanisms.

Eisenberg in “Encyclopaedia of Applied Electrochemistry”(2012) and later in a Key note address in a: “Work shop on mathematical models of Electrolytes applied to molecular biology, (2012)” , at National Taiwan University, Taipei on ‘Ions Come in Pairs’, and a second talk on ‘Ion channels are the Valves of Cells’, observed that ‘Ions in water are the liquids of life that are not ideal solutions ; Law of mass action assumes that nothing interacts. Force Fields are calibrated ignoring interactions with ions but chemically specific properties come from interactions in Ionic solutions. Molecular Dynamic Simulations involving force fields always assume no interactions. In an electric field every ion interacts with every other ion through the Ionic atmosphere which is crowded around central steric effects. No theory is available for mixture of Ions. Flow of the ions is yet to be incorporated. Hence the Law of mass action must be replaced by a Variation principle.’ Most of these findings form the inspiring thoughts for the work pursued and reported in this thesis.

RTILs constitute a big arena of research pursued in the field of synthesis and Ethylene Glycol (EG) has several applications in its utility in the Enzymology. Several

Reviews pointed out the specialities of EG in this field. In the book entitled “Superconductors- Materials, Properties and Applications” (2011) , edited by Alexander Gabovich, wherein Gunzi Saito and Yukihiro Yoshida presented a lot of information about the usage of Cu ion in the superconducting materials as a viable alternative for Au and Ag ions. RTILs with magneto- active inorganic and organic ions are the current topic of active research on the international platforms especially in regard to superconducting materials. These considerations evoked the interest on Ionic liquid systems in the present study. Having chosen the RTILs with Cu ions involved with them, a systematic probing into the matter, to be continued as far as possible and forms the focus of this thesis.

A detailed survey is attempted with this intention under the guidance of V. Brahmajirao (Andhra University Ph.D., Thesis of the year 1977) and the work started with the dielectric measurements and application of the Glueckauf’s model to the relative permittivity data evaluation of Ionic liquids. The basic Debye- Huckel Model (DHM), proposed the existence of the Ionic atmosphere, around every central ion, but neglected the influence of the charged ions on the medium, which was treated as a dielectric continuum of constant electrical interactions. The Coulomb’s law demands a lowering in the relative permittivity of the solvent into which ions enter to form Ionic liquid. Later Glueckauf developed a mathematical model for this lowering. In the present study, Glueckauf’s Model of Lowering of Dielectric Constant (GMLDC) has been taken into account and established its experimental validity by Dielectric measurements with Operational Amplifier Technique. This forms the content of the dielectric studies reported in the thesis by the author. Later the historic Pitzer model inspired the author to which the data was applied. This was done because the bulk of the data, as seen from the literature was apparently applied by several workers to the Pitzer model, and was bringing out several interesting findings.

The Nobel Prize winning “Eigen and Tamm Ion Pair formation Mechanism”, (ETIPM) was studied vigorously by Barthel, Buchner, Hefter, Marcus and Chandrika Akilan, Brahmajirao and Thirumaran etc., in several perspectives. Of this, C. Akilan studied ETIPM in Copper Sulphate Ionic liquids, using certain techniques. In the present study, these techniques are supplemented with Dielectric, Thermodynamic and Acoustic studies and found an excellent agreement with those of C. Akilan.

The Acoustic, Densimetric, Refractive Index determinations reported in this thesis are performed by most advanced 'ANTONPAAR' (Austrian made) experimental technique. All the above mentioned parameters are determined for a set of five temperatures with this setup. The setup is totally automatic and internally programmed to record the data into the hard disc using a software provided by the manufacturer. Several advanced features of the setup are discussed in the chapter 'Experimental Techniques'.