

Local structure in mixtures of ionic liquid with molecular solvent: vibration spectroscopy, NMR and molecular dynamics simulation

Abdenacer Idrissi

Univ. Lille, CNRS, UMR 8516- LASIRE, Laboratoire Avancé de Spectroscopie pour les Interactions, la réactivité et l'Environnement, F-59000 Lille, France

Abstract

Ionic liquids (IL), being low-temperature melts by their nature, are of considerable scientific interest due to a number of their unique properties. The practical application of ILs, especially in electrochemistry, has significantly expanded due to the use of mixtures with molecular solvents of various natures. A detailed microscopic description of the local structure in such systems, depending on the nature of its constituent components and the composition of the mixture, remains an urgent problem of modern chemistry of liquid state. In this chapter, we review the results obtained by vibration spectroscopy and NMR chemical shift on the variations in microscopic structure as a function of mixture composition. We point out the controversy about the assignment of the imidazolium C-H stretching vibration mode and systemized its red shift as associated with the outcome of the competition of the solvent molecules and the anions for the C-H bond. Furthermore, the introduction of the double difference relative chemical shift helps us to compare and rationalize the ^1H chemical shift literature data obtained in various ionic liquid/solvent mixtures. The most significant changes in the ^1H chemical shift occur at low ionic liquid content. Dilution and stacking interactions between the cation rings induce negative variation of the ^1H relative chemical shift. As the solvent and the ions can establish hydrogen bond interactions, when these interactions are weaker, almost equal or higher than the interionic interactions, this results in negative, almost equal to zero or positive values of the relative chemical shift, respectively.

Moreover, starting from the idea that the nearest neighbor anions or solvent molecules of the C-H bond are strongly influencing the associated C-H vibration mode and the ^1H chemical shift, we used molecular dynamic simulation and the nearest neighbor approach to calculate radial distribution and spatial radial distribution functions, and to define two statistical distance descriptors of the hydrogen bond structure C-H... X (X being atom of either the anion or of the solvent) to characterize the local structure around the C-H bond of the cation. The mole fraction dependence of these statistical properties, calculated by taking only the nearest neighbor into account, correlates consistently with spectroscopic data. Indeed, these descriptors are relatively unaffected in the ionic liquid mole fraction (x_{IL}) range between 1.0 and 0.3, while with further decrease of x_{IL} a large effect on these descriptors is observed. These changes are compatible with the physical picture that the solvent molecules compete with the anions to occupy positions close to the cation ring hydrogen atoms. They are associated with the expected weakening of the cation – anion interactions in the chosen solvents. These results are in good agreement with the behavior of the ^1H chemical shift and the C-H vibration mode as a function of x_{IL} . Furthermore, the results of the MD simulations point out the importance of the anion – solvent interactions in weakening the interionic ones.

Biography



Abdenacer Idrissi received his M.Sc. in Physics from the University of Mohammed I (Oujda, Morocco), and his PhD in Physical Chemistry from the University of Lille (France), where he is a Professor of Chemistry and Physics at the present time. His research interest is focused on the understanding of the structure and dynamics of fluids including ionic liquids and supercritical fluids. The main problematics are the understanding of the cellulose dissolution, the control of the polymorphic forms of the bioactive molecules and the characterization of the short time dynamics of the dyes used in solar cells. These research are carried out using a combination of an array of spectroscopic technics (IR, Raman, neutron scattering, time resolved spectroscopy) with molecular dynamics simulation.