

Hydrogen bonding interactions in ionic liquids and in their mixtures with molecular solvents

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The analysis of the hydrogen bond interactions becomes more complicated when the IL is mixed with a molecular solvent. Indeed, to overcome the high viscosity of the ILs, they are mixed with molecular solvents that induce a modulation of its overall physical chemical properties (viscosity, density, conductivity, melting temperature, surface tension ...) with a large changes occurring at low IL mole fraction x_{IL} below 0.2. Then the understanding of the interactions, and in particular the hydrogen bonding ones, that exist between the component ions of IL and the molecular solvent is essential for the proper use these mixture in industrial application. For this purpose, in a first stage, we investigated, using molecular dynamics simulation, the hydrogen bonding interactions in the 32 types of imidazolium based ionic liquids combined with various type of anions.^{1,2} In a second stage we investigated, the change of the hydrogen bond distances characteristics in four 1-butyl-3-methylimidazolium cation based ionic liquid combined with four perfluorinated anions in a mixture with three molecular solvents. In order to assess the changes of the hydrogen bonding interactions as a function of the anion type as well as to evaluate the effect of the IL mole fraction in a mixture, x_{IL} , charge distribution model on these interactions, we introduce here a double distance characteristic of the hydrogen bonding arrangement, D-H...A, of the donor moiety, D, the bonding H atom, and the acceptor atom, A. In the case of a linear hydrogen bond, which is qualified as strong one, the d_2 distance is equal to the sum of the intramolecular D-H and intermolecular d_1 distances. On the other hand, in the case of a bent, weaker hydrogen bond, the d_2 distance is noticeably shorter than the sum of the D-H and d_1 distances, and the hydrogen bond angle, θ , can be estimated from the law of cosines. These distances are associated with the average distances calculated from the nearest neighbor distributions of the A atom around the H and D atoms.³ The results show that the cation-anions interactions are correlated with the hydrogen bonding strength as analyzed from the distance and angle characteristics and are dependent on the size of the anion and its collective interaction with various hydrogen atoms of the cation (including those of the methyl and butyl chains), while in the mixture the rate of weakening of the cation-anions interactions with dilution is associated with the rate of strengthening of the anion-solvent interactions.

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