Nanostructuring in Pure Ionic Liquids Investigated by Molecular Simulation

A.A.H. Padua[1,C,S], J.N.A. Canongia Lopes[2] and M.F. Costa Gomes[1]

[1]*Laboratoire de Thermodynamique des Solutions et des Polymères, Universite Blaise Pascal Clermont-Ferrand/CNRS, Aubiere, France*
agilio.padua@univ-bpclermont.fr

[2]*Centro de Quimica Estrutural, Instituto Superior Tecnico, Lisboa, Portugal*

Structural and thermodynamic properties of ionic liquids were studied by computer simulation using a molecular force field developed specifically for these substances. In certain pure ionic liquids, it was observed that the liquid phases are not random nor identical to simple molten salts, whose structure is essentially defined by charge ordering. In room-temperature ionic liquids, which are composed of large anisotropic cations, nanometer-scale structuring is observed in simulations. For alkylmethylimidazolium ionic liquids with alkyl side chains longer than or equal to butyl, segregation is observed between, on one side, the strongly charged parts of the cations and the anions, and on the other, the non-polar side chains. The alkyl chains aggregate in non-polar domains that permeate a tridimensional network of ionic channels formed by the anions and by the imidazolium rings of the cations. The nanostructures can be clearly visualised by tagging the atoms belonging to the two types of domain, and the ionic liquids become analogous to systems exhibiting microphase separation. As the length of the alkyl chain increases the non-polar domains become larger, increasingly connected, and cause swelling of the ionic network. The systems discussed have side-chains shorter than dodecyl; for longer chains the ionic liquids form liquid crystals. Such microsegregation has important consequences to the equilibrium and dynamic properties of the ionic liquids. The nature of the interactions of nonpolar and polar solutes with these solvents is investigated by free energy calculations, and the solubilities from simulation are compared to experimental measurements.