

Critical and Non-Critical Mesoscopic Inhomogeneities in Solutions of the Protic Ionic Liquid Ethyl Ammonium Nitrate and pentanol

Olga Russina

Dipartimento di Chimica, Università di Roma Sapienza, Rom, Italy

Wolfram Schroer^{C, S}

Fachbereich Biologie-Chemie, Universität Bremen, Bremen, Germany
schroer@uni-bremen.de

Bernd Rathke

Technische Thermodynamik, Universität Bremen, Bremen, Germany

Alessandro Triolo

Istituto Struttura della Materia, Consiglio Nazionale delle Ricerche, Rome, Italy

Mesoscopic inhomogeneities in binary mixtures of ethyl-ammonium nitrate (EAN), a protic ionic liquid, and pentanol are investigated using Small Angle X-ray Scattering as a function of concentration and temperature ranging from 193 to 313 K. Both compounds are amphiphilic and characterized by an extended hydrogen bonding network; however, though macroscopically homogeneous, their mixtures are heterogeneous at the mesoscopic spatial scales. Two different species of mesoscopic inhomogeneities are observed: Critical concentration fluctuations, as observed in EAN/Octanol mixtures [1], and inhomogeneities caused by separation into ionic and non-ionic regions. The latter ones have been predicted by simulation [2] and verified experimentally [3] in ionic liquids containing cations with long hydrocarbon chains. In pure EAN such structuring into ionic and non-ionic regions gives rise to a band centred near $Q = 6.2 \text{ nm}^{-1}$ [4]. A similar band at $Q = 5.2 \text{ nm}^{-1}$ is also observed in pentanol, suggesting a segregation into polar and non-polar regions. In mixtures the inhomogeneity bands of EAN and pentanol match. When approaching the critical composition near the mole fraction $x = 0.5$ and lowering the temperature towards the critical temperature, the inhomogeneity band merges with a band centred at $Q=0$ that increases, when approaching the critical region. The concentration and temperature dependence of the $Q=0$ band have the characteristic features for critical fluctuations near the liquid-liquid upper critical solution point, and is thus attributed to critical concentration fluctuations. The critical temperature is estimated by extrapolation to $T_c \approx 190 \text{ K}$, which is located inside the solid phase and thus cannot be reached in the experiment.

References

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