Critical and Non-Critical Mesoscopic Inhomogeneities in Solutions of the Protic Ionic Liquid Ethyl-Ammonium Nitrate and *n*-Alkyl Alcohols

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Mesoscopic heterogeneities in binary mixtures of the protic ionic liquid ethyl-ammonium nitrate (EAN) with alcohols (pentanol, hexanol, and heptanol) are investigated using Small Angle X-ray Scattering as a function of concentration and temperature ranging from 193 to 313 K. Measurement of the phase diagrams characterize the thermodynamic space of the systems. Alcohols and EAN are amphiphilic and characterized by an extended hydrogen bonding network; however, though macroscopically homogeneous, their mixtures are heterogeneous at the mesoscopic spatial scales where two different species heterogeneities are present: Critical concentration fluctuations centered at q=0, known from EAN / Octanol mixtures, and heterogeneities caused by segregation into ionic and non-ionic regions. The latter ones were predicted by simulation and verified experimentally in ionic liquids containing cations with long hydrocarbon chains. In pure EAN, such structuring into ionic and non-ionic regions is observed as well giving rise to a band centered near q = 6.2 nm⁻¹. A similar band at = 5.2 nm⁻¹ is also observed in alcohols, again suggesting a segregation into polar and non-polar regions. Those heterogeneity bands of EAN and alcohols merge in mixtures. When approaching the critical composition near the mole fraction x = 0.5 and lowering the temperature towards the critical temperature, critical concentration fluctuations with a band centered at q=0 dominate and overshadow the ionic-non-ionic heterogeneity band. The concentration and temperature dependence of the q=0band have the characteristic features for critical fluctuations near the liquid-liquid upper critical solution point, and is thus attributed to critical concentration fluctuations. In the case of the pentanol system, the critical solution point is virtual as it lays inside the solid phase region ($T_c \approx 190$ K) and cannot be reached in the experiment.