

## The Behavior of KI Dissolved in Supercritical Ammonia

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The knowledge of the dependence of thermodynamic and structural properties of dilute solutes on the solvent's molecular density ( $\rho_l$ ) is of importance on two accounts: it gives a valuable insight into solvation phenomena, and it provides useful information for the increasing number of processes that employ supercritical solvents. It is particularly relevant in the case of systems with strong solute-solvent interactions where solvation plays a prominent role, e.g. ionic solutes dissolved in polar supercritical solvents. We have studied thermodynamic and UV-spectroscopic properties of KI in supercritical ammonia (SCA) at 420 K, and also have done some measurements at subcritical temperatures. The use of the supercritical solvent allowed us to identify two spectroscopically active species in the solutions which correspond to various stages of ion pairing controlled by fluid density. The complementary use of simulation and electronic structure calculations enabled us to make a detailed description of the role of solvent molecules on the properties of the solutions. It was established that for KI contact ion pairs in SCA there are two solvation regions with very different dependences of the solution's equilibrium properties on reduced density  $\rho_{\text{red}}$ . This marks a striking difference with the known behaviour of systems having weaker solvent-solute interactions. For ions dissolved in polar supercritical solvents, like ammonia and water, it is necessary to establish the fluid density dependence of properties from the solute vapour to liquid-like solutions in order to enable bridging the behaviour found in bulk solvents and in clusters with that of the gaseous solute ( $\rho_{\text{red}} = 0$ ). The fact that the solvation of the contact ion pair in SCA at reduced density  $\rho_{\text{red}} = 0.2$  already determines its behaviour at higher density is remarkable.