Lower Critical Solution Temperatures of Hydrofluorocarbon + Room-Temperature Ionic Liquid Solutions

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According to our recent solubility studies on 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) with various hydrofluorocarbons (HFCs) [1], the [bmim][PF_6]-rich side solution shows a very high solubility (far more soluble than any other compounds studied so far with ionic liquids), but the HFC-rich side solution exhibits partial immiscibilities with lower critical solution temperatures (LCSTs). This indicates type V mixture behavior according to the van Konynenburg-Scott classification [2]. This behavior is quite interesting and in contrast with ionic liquid solutions of various alcohols [3], where immiscibility gaps have been well studied experimentally and show upper critical solution temperatures (UCSTs). UCSTs are more commonly observed behaviors for phase separation (liquid-liquid demixing), as predicted by the well-known regular solution theory. Various types of liquid-liquid demixing in non-electrolyte solutions are known to exist, such as LCST, UCST, closed demixing curve, and their combinations. Therefore, the present phase behaviors are not unique in nature solely due to the electrolyte (ionic liquid) solution, although there might exist some speciation effects (due to electrolyte dissociations) and/or special ionic interactions. In this report, we are particularly interested in the observed LCST behavior of HFC [bmim][PF_6] mixtures and investigate the general behavior of liquid-liquid demixing using some statistical mechanical models (or extended lattice-fluid models) [4], which can describe LCSTs with hydrogen-bonded (or directional intermolecular interacting) mixtures. The present study may shed some light on the observed phase behaviors with unique intermolecular interactions such as hydrogen bonding between HFCs and ionic liquids.

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