Origins of Symmetry in Polymer Ionic Liquid Phase Diagrams

JANE LIPSON, RONALD WHITE, Dartmouth College — Recent experimental work [Lee et al. Macromolecules 45, 3627 (2012)] reveals rather symmetric looking coexistence curves for poly(ethylene oxide) in [EMIM][BF$_4$]. This is in marked contrast to solutions involving non-ionic solvents, which show a characteristic and strong asymmetry, correlated with the molecular weight disparity between the two components. Using our simple theoretical approach we show that the special character of this systems derives from two thermodynamically-based properties. First, we find that the ionic solvent has a considerably stronger cohesive energy densities than non-ionic counterparts. In addition, we propose that aggregation in the ionic liquid has a significant impact on the entropy of mixing, typically a strong driving force for miscibility in polymer solutions. In this talk we explain how each of these features serves to drive the critical composition to the middle of the phase diagram.

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