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Salting-out and Salting-in in Polyelectrolyte Solutions PENGFEI ZHANG, Division of Chemistry Chemical Engineering, California Institute of Technology, JIANZHONG WU, Department of Chemical and Environmental Engineering, University of California, Riverside, ZHEN-GANG WANG, Division of Chemistry and Chemical Engineering, California Institute of Technology — The phase behavior of polyelectrolyte (PE) solutions is governed by complicated interplay involving the mixing entropy, excluded volume, chain connectivity, and electrostatic interactions. Here we study the phase behavior of PE solutions in both salt-free condition and with added salt using a liquid-state (LS) theory based thermodynamic model. The LS model accounts or the hard-core repulsion by the Canahan-Starling equation of state, correlations due to chain connectivity by the first-order thermodynamic perturbation theory, and electrostatic correlations by the mean-spherical approximation. In comparison to the prediction from the well-known Voorn-Overbeek theory, the LS model predicts loop-type binodal curves in the salt-PE concentration diagram at temperatures slightly above the critical temperature of PE solution in salt-free case, consistent with the experimental study. The phase separated region shrinks with increasing temperature. Three scenarios of salting-out and salting-in phenomenon are predicted with addition of salts based, depending on the PE concentration.

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