Scaling Crossover Description of Near-Critical Vapor-Liquid Equilibria in Aqueous Solutions of Sodium Chloride

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An adequate interpretation of experimental data in binary fluids near the vapor-liquid critical point is complicated by an interplay between two different crossover phenomena: crossover between pure-fluid-like behavior and mixture-like behavior; and crossover from Ising-like asymptotic scaling behavior to mean-field behavior. Moreover, in ionic systems possible dissociation-association processes cause additional complications. We present a quantitative description of experimental data for vapor-liquid equilibria, critical locus, and isochoric specific heat capacity of near-critical aqueous solutions of sodium chloride in terms of a crossover model based on the extended principle of critical-point universality. We have analyzed existing experimental data on coexisting concentrations and densities along isotherm (above the critical point of water) in a wide range of pressures (from the critical pressures P_c to $P/P_c \approx 0.5$), and isochoric specific heat capacity data along critical isochores. It is shown that the critical phenomena in this system are characterized by a crossover from Ising-like asymptotic behavior to mean-field behavior and by a decrease of the Ising-like asymptotic critical region with increase of sodium chloride overall concentration. However, the model is inadequate at the lowest overall concentrations that may be due to dissociation-association effects.

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