Modeling Mixed Solvent Electrolyte Solutions Using a Cubic Equation of State

L.A. Watts
Physical and Chemical Properties Division
National Institute of Standards and Technology
Boulder, CO 80303 USA

Accurately predicting the phase behavior of aqueous-organic solutions is difficult, and the addition of a salt makes the system even more non-ideal. A model for mixed solvent electrolyte solutions is developed from the Peng-Robinson-Stryjek-Vera (PRSV) equation of state using the Wong-Sandler mixing rules. The modification of Stryjek and Vera to the Peng-Robinson equation of state improved its modeling of non-ideal compounds. The result for a mixture is strongly dependent on the mixing rules used. The non-random two liquid (NRTL) model of Chen for electrolyte solutions with temperature dependent parameters is employed to provide the excess Gibbs energy and the high pressure activities required for the Wong-Sandler mixing rules. The model requires only pure component and binary interaction parameters. The model has four parameters (two are temperature dependent), and produces a quadratic second virial coefficient (useful for the vapor phase only). This model is applied to the system water-ethanol with various salts added over a wide range of temperature. The model is able to accurately predict the vapor composition and pressure given the liquid composition and temperature, and correctly models the effect of salt addition on the azeotrope (azeotrope breaking). The potential for other applications is discussed.