Modeling Phase Separation in Water-Solvent-Electrolyte Mixtures

T.N. Rogers,[C,S] D.J. Wiegand, and M.E. Mullins
Dept. of Chemical Engineering, Michigan Technological University, Houghton, MI, U.S.A.
tnrogers@mtu.edu

To properly represent a nonideal mixed-solvent liquid phase containing an electrolyte (e.g., a dissociating salt), an activity coefficient model must simultaneously represent the electrostatic forces between the ionic species, as well as all other ion-molecule and molecule-molecule interactions. Models such as Electrolyte NRTL [5] presume local homogeneous mixing of all components and ions in a given phase, so this representation is flawed when ions are incompletely solvated in a predominantly organic solvent. For example, when MEK-rich and water-rich liquid phases are in equilibrium, the MEK-rich phase contains only a limited amount of water (0.08 mole %), making salt ion solvation problematic, and violating this basic premise.

In isothermal liquid-liquid flash calculations involving water and an organic co-solvent, a salt will distribute at very different concentrations in the two equilibrium phases, since the ionic species usually have a much greater affinity for water. However, Electrolyte NRTL sets the equilibrium salt concentrations to be identical in the two phases, and the reference state for the ionic species in the co-solvent phase is chosen to be the infinitely dilute state in water, in order to avoid the complication of using a solvent-based reference state [1, 5]. Moreover, the salt's activity coefficients in both liquid phases are functions of temperature and composition only, and cannot be numerically equal, which equal salt concentrations would require.

To enhance the Electrolyte NRTL model's representation of predominantly solvent solutions, this work attempts to better account for the hydration layer surrounding the ionic species in such phases. Ion-solvent interactions are derived from a modification [3] of the original Born equation [4]. This approach was applied and evaluated for ternary water-solvent-salt VLE and LLE data measured collaboratively by MTU and NIST researchers in a previously published study [2]. Vapor-liquid-liquid equilibrium data were available for three ternary water-solvent-salt mixtures consisting of sodium nitrate salt at various concentrations in aqueous solutions of acetone, isopropyl alcohol, and methyl ethyl ketone. The miscibility of each organic solvent in water is modeled, in this work, as a function of sodium nitrate concentration.

[1] C.C. Chen and L.B. Evans, *AIChE J.* **32**, 444 (1986).
[2] L.A. Watts and C.D. Holcomb, *Measurements and Models for Hazardous Chemical and Mixed Wastes*, Final Report to U. S. Department of Energy, NIST, Boulder, CO, 2002.
[3] A.A. Rashin and B. Honig, *J. Phys. Chem.* **89**, 5588 (1985).
[4] M. Born, *Z. für Physik.***1**, 45 (1920).
[5] Y. Liu and S. Wattanasiri, *Fluid Phase Equilibria* **116**, 193 (1996).