

Vapor-Liquid-Liquid Equilibria of Hydrofluorocarbons and 1-Butyl-3-Methylimidazolium Hexafluorophosphate

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Recently, we have measured gaseous solubilities (vapor-liquid equilibria) of various hydrofluorocarbons (HFCs) in room-temperature ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF₆], using a gravimetric microbalance at temperatures from 283 to 348 K and pressures from 0.01 to 2 MPa [1]. Vapor-liquid equilibrium (VLE) data have been successfully correlated with a modified Redlich-Kwong equation of state (EoS), which was developed earlier for non-electrolyte solutions such as refrigerant lubricant oil mixtures [2]. The present EOS predicts partial immiscibilities with lower critical solution temperatures (LCST) in the HFC-rich side solutions and indicates the Type-V mixture behavior, based on the Konynenburg-Scott classification. In order to verify our EOS predictions, we have conducted experiments to show vapor-liquid-liquid equilibria (VLLE) for some selected HFCs (R-23, R-41, R-125, R-134a, R-143a, R-152a, and R-161) [bmim][PF₆] mixtures. VLLE data have been obtained using a “volume-mass-measurement” method at various isothermal conditions, which was developed in this study. According to the Gibbs phase rule, VLLE of a binary system is a univariant state. This means that at a given intensive variable, say temperature, there is no freedom for other intensive variables; all other variables such as compositions, pressures, or densities of the system are uniquely determined regardless of any different extensive variables (volume of each phase and total mass of the system). A set of two volume-and-mass measurements at a given isotherm provides compositions and liquid densities of each phase, by solving a set of linear algebraic equations without any help of analytical methods for the composition analysis. The present method was tested by the use of a known VLLE binary system: 2-butanol water. The predicted and observed VLLE are compared and the validity of the present EOS method will also be discussed.

[1] M.B. Shiflett and A. Yokozeki, *AIChE J.* (2005) (in Press).

[2] A. Yokozeki, *Int. J. Thermophys.* **22**(4), 1057 (2001).