A Molecular Formulation of the Activity Coefficients and Their Reference Fugacities for Supercritical Fluid States

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It is well-known that the activity coefficients in the Lewis-Randall approach are based on the judicious choice of a reference fugacity, f_{i0}. Usually this f_{i0} is chosen to be the pure state fugacity of component i at the system temperature T_0, system pressure P_0, and the same state (liquid or vapor state)— i.e., in the symmetric convention. However for mixtures of components, several of which find themselves to be in a supercritical state, given the system temperature T_0, the reference state becomes problematic: at $T_0 > T_{ci}$ (the critical temperature of component i), pure i does not exist as a liquid, and there is no pure liquid f_{i0} to act as the reference state. Worse scenarios are when the condition falls in the two-phase region, metastable or spinodal. An alternative is to use the asymmetric convention with Henry's law constants. A direct chemical potential formula has been proposed earlier (L. L. Lee 1992[1]) based on the molecular correlation functions. With this formula, the classical activity coefficients in either conventions can be expressed in terms of the densities of the mixtures and pure components, or alternatively the system pressure and compressibility factors, plus the molecular correlation functions (such as the cavity functions, pair correlations, bridge functions, and the star functions). The asymmetric convention involves additionally the chemical potentials at infinite dilution (as the Henry's constants necessarily implicate thusly). These formulas are here applied to the vapor-liquid equilibria of a high pressure hydrocarbon mixture of methane and n-pentane (68.9 bar and 444 K), where methane is the supercritical fluid. We use both molecular dynamics simulation and Ornstein-Zernike integral equations with a ZSEP-type closure for this study. Results obtained are accurate as compared with the experimental data from Sage and Lacey[2]. To achieve more cogent agreement with the molecular expression, an alternative reference fugacity, different from the traditional ones, is proposed that obviates the difficulties associated with the non-existence of a supercritical liquid state. The activity coefficients are now directly aligned with Lee's direct chemical potential formula. For components in a mixture, supercritical or subcritical, this new standard state fugacity is always well defined and "calculable" at the system T_0 and P_0, and is no longer fictitious. The results are general, and can be applied to any components in a supercrticial mixture.

[1] L.L. Lee, J. Chem. Phys., **97**, 8606-16 (1992).
[2] H. Sage and W.N. Lacey, Monograph on API Research Project, **37** (1950).