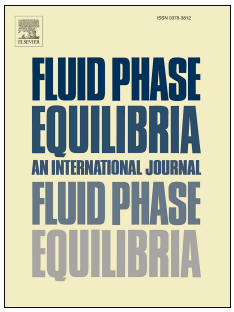

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Evaluation of Equations of State for Simultaneous Representation of Phase Equilibrium and Critical Phenomena

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Abstract

Precise description of the critical points with association equations of state requires rescaling of the parameters to match experimental critical temperature and pressure of pure components. In this work we developed a method to include critical data restrictions in the parametrization procedure of the Cubic-Plus-Association (CPA) equation of state (*EoS*). We obtained new parameters for methanol and alkanes from n-hexane to n-decane. The comparison with the original parameters showed that this procedure is important for associating compounds, since for inert species the equation reduces to the Soave-Redlich-Kwong (*SRK*) *EoS*. The application of the rescaled parameters improved the critical point representation of pure fluids at the expense of the saturated liquid phase volume description. In the case of binary mixtures containing methanol and n-alkanes, the association model with the new parameters satisfactorily predicted the experimental critical data, indicating the importance of the rescaling parametrization procedure in the computation of the critical pressure and temperature for systems with associating species. Both sets of CPA parameters gave similar deviations in the bubble point pressure and vapor composition for the vapor-liquid equilibrium calculations. However, the rescale parameters gave rise to larger deviations in the composition of the polar rich phase in the liquid-liquid equilibrium.

Introduction

The correct representation of the critical properties of pure and multicomponent systems is essential for several engineering applications in different industries. In the energy sector, the utilization of supercritical n-hexane as a solvent for the production of methanol from syngas is becoming more attractive due to high conversion rate and enhanced heat and mass-transfer efficiencies [1]. Recent studies also show the advantages of using alcohol in near/supercritical conditions to produce bio-fuel [2, 3]. In the oil and gas industry, the correct description of the reservoir fluids with high carbon dioxide content under high pressure and high temperature conditions is crucial for the successful implementation of Enhanced Oil Recovery projects [4]. Finally, in pharmaceutical, food and textile industries, fluids in the near/supercritical regions are already applied in different processes such as the synthesis of new materials and catalyst supports, like aerogels, special separation techniques, e.g. supercritical fluid chromatography, and the extraction processes of non-volatile components, like caffeine from green coffee beans [5, 6].

The reason that supercritical fluids are employed in such a range of operations is due to the unique characteristics that they possess near and above the critical point. In regions above the critical point, a fluid exhibits gas-like viscosity and diffusivity, but also liquid-like density and solvating properties, making it an excellent solvent [5]. In the vicinities of the critical point, a fluid is characterized by the presence of large-scale density and composition fluctuations [7, 8], thus small changes in operation conditions lead to substantial modifications in the ability of a fluid to selectively dissolve non-volatile substances [9].

Due to the singular behavior of a fluid near the critical point, classical equations of state (*EoS*) fail to correctly describe the thermodynamic properties [10, 11]. Furthermore, the parameters of molecular based *EoS* are typically regressed from vapor pressure and saturated liquid phase volume data over a reduced temperature range between 0.5 and 0.9 or 0.95 [12], without imposing any constraints to the critical constants. Therefore, the association models usually over-predict the critical temperature and pressure of pure components, which result in qualitatively incorrect representations of pressure-composition phase diagrams near the critical point [13].

In order to improve the description of systems in conditions not far from critical point, without resorting to non-mean-field models, it is necessary to rescale the molecular based *EoS* pure compound parameters to match the critical temperatures and pressures [14]. In the case of the *SAFT-VR EoS*, Galindo and Blas [15, 16] rescaled the size and energy parameters to improve the critical region representation, while maintaining the third dimensionless parameter from the original set. Cismodi et al. [14] developed a parametrization technique by modifying the *PC-SAFT EoS* into a