Crossover HR-SAFT Equation of State for Fluid Mixtures: Application to Binary Mixtures of Carbon Dioxide, Water, and Methanol

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In this work, we extend the crossover statistical associating fluid theory (SAFT) equation of state (EOS), developed earlier for one component fluids [1], to fluid mixtures. Using a general, based on the renormalization group theory approach for transforming an analytical equation of state (EOS) into the crossover form [2], we firstly developed the crossover SAFT EOS for pure CO_2, H_2O, and methanol, which incorporates non-analytic scaling laws in the critical region and is transformed into the analytical, classical HR-SAFT EOS originally developed by Huang and Radosz [3] far away from the critical point. In addition to the classical HR-SAFT parameters, the crossover HRX-SAFT EOS contains a Ginzburg number as an input but yields a much better representation of the thermodynamic properties of pure fluids than the original HR-SAFT EOS. Here, similar to our previous work for n-alkanols [1], carbon dioxide, water, and methanol are modeled as associating chain molecules with two association sites, i.e. model 2B [3]. In all substances, the HRX-SAFT EOS reproduces the saturated pressure data in the entire temperature range from the triple point to the critical temperature with the average absolute deviation (AAD) of about 1%, the saturated liquid and vapor densities with an AAD of about 2%, and the values of pressure in the one-phase region with AAD of about 2-3%.

In the second step, using the classical mixing rules in terms of composition, we developed the HRX-SAFT EOS for binary mixtures. For the crossover function in binary mixtures, we used the simplified representation as employed earlier by Kiselev and co-workers in the crossover cubic EOS [4,5]. For the non-association terms in the classical HR-SAFT, we used the vdW1 mixing rules, as described in [6], with one constant binary interaction parameter (k_{ij}). For the association term in the classical HR-SAFT, we assumed that in mixtures there is cross association between the O type in carbon dioxide molecule and the H type in the methanol and water molecules. For estimating the fractions of non-bonded molecules in the associating term we used a generalized procedure developed recently by Tan et al. [7]. The HRX-SAFT has been tested against extensive experimental data sets for the VLE, PVTx, and excess properties in carbon dioxide + water, carbon dioxide + methanol, and water + methanol mixtures.

We show that the HRX-SAFT EOS not only yields a better description of the PVTx and VLE properties of binary mixtures in the critical region, but also improves the representation of the entire thermodynamic surface. Unlike the original HR-SAFT EOS for binary mixtures [7], the HRX-SAFT EOS is capable of simultaneous representation of the pressure-composition, pressure-density, and density-composition isotherms in binary mixtures with a high accuracy. The short comings of the HRX-SAFT EOS in the representation of the asymptotic critical region of binary mixtures with the simplified formulation for the crossover function [5] are also discussed.

[1] S.B. Kiselev, J.F. Ely, H. Adidharma, M. Radosz, *Fluid Phase Equilibria*, **183-184**, 53 (1998).
[2] S.B. Kiselev, *Fluid Phase Equilibria*, **147**, 7 (1998).
[3] S.H. Huang and M. Radosz, *Ind. Eng. Chem. Res.* **29**, 2284 (1990).
[4] S.B. Kiselev and D.G. Friend, *Fluid Phase Equilibria*, **155**, 33 (1999).
[5] S.B. Kiselev and J.F. Ely, *J. Chem. Phys.*, **119**, 8645 (2003).
[6] S.H. Huang and M. Radosz, *Ind. Eng. Chem. Res.* **30**, 1994 (1991).
[7] S.P. Tan, H. Adidharma, M. Radosz, *Ind. Chem. Eng. Res.* **43**, 203 (2004).