148n Generalized Equation of State for the Perturbed-Chain Statistical Associating Fluid Theory

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A generalized molecularly-based equation of state not only provides a useful thermodynamic basis for phase equilibrium calculations but also allows for characterizing the effects on a molecular structure and its interactions on bulk properties and phase behavior. The statistical associating fluid theory (SAFT) was extended to some real molecular fluids in which the practical calculations require three substance-dependent parameters for nonassociating substance; specific interactions, such as hydrogen bonding, are characterized by more two association parameters for a specific molecule. The SAFT equation of state proved a significant improvement over more empirical equations of state, and has a firmer basis in its inclusion of chain and association effects in the reference term. As a result it gives better results for associating and chain-molecule fluids. Such calculations are typically eight or nine orders of magnitude cheaper, and about six orders faster, than an experimental phase-equilibrium measurement for a binary mixture. Many modifications of the SAFT model has been suggested over the years, based on the SAFT as a reference with applying Barker and Henderson's second-order perturbation theory, Gross and Sadowski developed the perturbed-chain SAFT equation of state, in which a hard-chain reference was considered in the perturbation theory leading to a dispersion term that properly depends on the chain length of a molecule. Compared to the SAFT version of Huang and Radosz, the PC-SAFT model was found to improve pure-component representation, in which the molecule-dependent parameters, such as segment number, segment volume, segment-segment interaction energy are required for nonpolar substances, and more two association energy and volume are further needed for a associating molecule. Since only limited molecules were provided for these specific molecule-dependent parameters, the application is expected to the other substances than those whose parameters are available. The corresponding-states principle provides a useful method to correlate the properties and also to represent the physical behaviors; as a result, in this work we apply the extended corresponding-states method into the PC-SAFT so that it is to obtain a general SAFT equation of state after its combination with the corresponding-states principle. The perturbed-chain statistical associating fluid theory (PC-SAFT) is consequently developed into a general equation of state in which the three pure-component parameters required for nonpolar molecules and five pure-component parameters for associating molecules are correlated by the extended corresponding-states theory. A comparison of the experimental vapor-pressure and liquid-density data for some representative molecules shows that the thermodynamic properties of any molecule may be predicted from this generalized PC-SAFT equation of state.