

An Equation of State for Acetic Acid Including a S.A.F.T Term

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Recently, the association term resulting from the S.A.F.T. theory [1] has been implemented in the traditional framework of empirical multiparameter equations of state [2, 3]. Here, as an exemplary application, we present an accurate EoS for acetic acid, which is known to be a strongly associating fluid. In the present model, the S.A.F.T term is combined with a conventional form; the latter roughly accounts for all effects not ascribable to association. The obtained equation represents experimental data generally within the scatter of the data. However, due to the limited quality of the available experimental data, accuracy requirements formulated for accurate technical equations of state [2] cannot be met all over the validity range of the equation. The presented model is able to foresee the anomalous trends of the heat capacity in vapor phase that are typical of strongly associating fluids. More accurate equations can be developed within the mathematical framework of the present model, provided supplementary data become available. Heat capacity data in the vapor phase at any density are vital for the tuning of the S.A.F.T. term. Some data of this kind are available for acetic acid, but they are generally lacking for other carboxylic acids such as formic, propanoic or butanoic acid. Further regularly distributed caloric data in the liquid phase would be very useful too. A systematic investigation of thermal decomposition for carboxylic acids and for other chemical substances is lacking in literature as well. The thermodynamic data set of acetic acid scatters very strongly beyond 520 K, and thermal decomposition is very likely to be responsible for this. Since the critical temperature is 590.7 K, no reliable data are available for the extended critical region, nor for supercritical states. Measurements of polar and associating fluids in the vapor phase are in any case very sensitive to decomposition effects and adsorption effects [4]. Another issue concerning carboxylic acids is that at low temperatures vapor pressures become very small. At these conditions measurements are hardly possible in the gas phase because of the very low density. Nevertheless strong associative effects are present even at such low densities, as it will be shown in this paper. Purely empirical terms cannot describe these effects due to the lack of accurate data. Thus, the inclusion of a physical term in multiparameter equations of state seems to be the most promising way to reach a meaningful thermodynamic representation of strongly associating fluids. The free parameters of the association term are tied to measurable physical quantities like the enthalpy and entropy change of the association reaction, so that a generalization to fluids pertaining to the same family can be easily achieved.