

Thermodynamic properties of water from SAFT and CPA equations of state: Critical assessment

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The performance of eight versions of the representative and most commonly used Statistical-Association-Fluid-Theory (SAFT) equations of state for water along with the Cubic-Plus-Association (CPA) equation are examined in detail both throughout the entire liquid phase region and at supercritical conditions. In addition to the temperature--pressure dependence of density, these response functions, the isothermal compressibility, isobaric heat capacity, and coefficient of isobaric expansivity, have been evaluated and compared with experimental data along five isobars ranging from $P=0.1$ MPa up to 1000 MPa, and along four isotherms from the melting point up to $T=750$ K. It turns out that to draw a general conclusion on the quality/accuracy of these equations is practically impossible with different equations predicting reasonably well different properties and at different thermodynamic conditions but failing in other instances. In general, the equations seem to be able to capture simple pressure dependence at isothermal conditions but fail primarily in estimating isobaric properties. All the equations (i) tend to perform reasonably well at pressures above the critical one where the excluded volume begins to predominate and the effect of hydrogen bonding becomes insignificant, (ii) but fail again at very high pressures, and (iii) have the most serious problems with predicting isobaric heat capacity. The most successful results are obtained from the recently developed Association Dependent PC-SAFT equation, which can be mainly attributed to its fitting using a broader set of experimental data compared to other equations; nonetheless, its performance still cannot be considered as overall reliable.