Abstract

A simple isotropic water-like model with two characteristic lengths in the pair potential was studied via the Ornstein-Zernike integral equation and Monte Carlo simulations. The radius of convergence using different closures (Percus-Yevick, hypernetted-chain, Kovalenko-Hirata, Rogers-Young, soft mean-spherical approximation) within the integral equations framework was evaluated, followed by determination of their accuracy in comparison with simulation data. Kovalenko-Hirata closure displays the broadest radius of convergence, while Rogers-Young proves more accurate as a result of the imposed thermodynamic consistency. Two critical points were determined analytically and from the simulation data. In addition to the ordinary gas-liquid critical point, a second liquid-liquid critical point was found at high pressure slightly above the temperature of melting, demarcating the range where two distinct liquid phases can coexist. The thermodynamic properties of the water-like model were calculated and were shown to describe well the anomalies that are typical of water, e.g. a temperature of maximum density and minimum of heat capacity. Hydration of non-polar solutes was modelled with the insertion of Lennard-Jones particles of various sizes and affinities for the solvent; typical characteristics of the hydrophobic effect were discovered. Furthermore, the model was extended to methanol. It was treated analytically with the reference interaction site model (RISM) integral equations, which are benchmarked against simulation data. In addition, the phase diagram of the methanol model contains two critical points. Based on experimental data for hydrogen bond strength and length in water and methanol, extrapolation from simulation data yielded the exact position of the liquid-liquid critical point in real methanol. Thermodynamics of the methanol model showed fewer anomalous properties than water, closely following the experimental trends. As aqueous solutions of methanol displayed pronounced non-ideality, the model predictions for excess volume and enthalpy of mixing were checked and found to successfully reproduce experimental data.

Keywords: molecular simulations, anomalous properties, water and methanol, isotropic models, liquid-liquid critical point