138g Molecular Modeling of Phase Behavior and Structural Properties for Acetone-Chloroform-Methanol Binary Mixtures

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Monte Carlo simulations in the grand canonical and isobaric-isothermal ensembles are used to investigate the phase behavior and structural properties of the binary mixtures acetone/chloroform, acetone/methanol and chloroform/methanol. These mixtures are of interest due to their complex phase behavior and hydrogen bonding interactions. Neat acetone and chloroform do not exhibit hydrogen bonding. When mixed, it is hypothesized that chloroform is able to form hydrogen-bonded complexes with acetone. The result is a minimum pressure azeotrope. Systems of acetone/methanol and methanol/chloroform should also exhibit significant hydrogen bonding interactions, however, neither displays a minimum pressure azeotrope.

New force fields, based on a non-polarizable Lennard-Jones (LJ) 12-6 plus point charge functional form are developed for acetone and chloroform. Point charges were determined from a CHelpG population analysis of the ab initio potential energy surface determined at the MP2/6-31g++ (3d, 3p) level of theory. LJ parameters were then optimized such that the liquid-vapor coexistence curve, critical parameters and vapor pressures are well reproduced by simulation. The new models yield improved vapor pressure estimates for the pure components, compared to existing force fields, and reproduce the minimum pressure azeotrope found in experiment for acetone/chloroform mixtures. The vapor pressures for the respective pure components were within 20% of the experimental values at T=308.32 K. The predicted azeotrope at xchloroform=0.77 is in good agreement with the experimental value of 0.64. The new models for acetone and chloroform were used to determine the pressure-composition diagrams for mixtures with methanol. The azeotropic composition of xacetone=0.57 for acetone/methanol and xchloroform=0.62 for chloroform/methanol were in good agreement with the experimental values of 0.51 and 0.68, respectively. NPT simulations at T=300K and P=1 bar were used to determine the microscopic structure of equimolar binary mixtures of acetone/chloroform, acetone/methanol and chloroform/methanol. Radial distribution functions show evidence of hydrogen bonding between acetone and chloroform, while existing force fields, such as OPLS and TraPPE, do not. A RDF and cluster analysis on acetone/methanol and chloroform/methanol configurations for all the force fields show methanol forms hydrogen bonded clusters (chains) with itself, but exhibits little hydrogen bonding with acetone or chloroform.