

Transferable Potentials for Phase Equilibria. 6. United-Atom Description for Ethers, Glycols, Ketones and Aldehydes

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Abstract

The extension of the transferable potentials for phase equilibria-united atom (TraPPE-UA) force field to the ether, glycol, ketone, and aldehyde functionalities is presented. New parameters for the ether oxygen, the carbonyl carbon (ketones), the carbonyl methine (aldehydes), and a special intramolecular hydrogen-bond term were fitted to the vapor-liquid coexistence curves for selected one-component systems. Coupled-decoupled configurational-bias Monte Carlo simulations in the Gibbs or grand canonical ensemble were used to compute the vapor-liquid coexistence curves for the neat systems of dimethyl ether, ethyl methyl ether, diethyl ether, dipropyl ether, diisopropyl ether, methyl *t*-butyl ether, 1,2-ethanediol, 2-methoxyethan-1-ol, 1,2-dimethoxyethane, 1,3-propanediol, acetone, 2-pentanone, 2-octanone, acetaldehyde, pentanal and octanal. Additional simulations were performed for the binary mixtures of diethyl ether + ethanol and acetone + hexane. Excellent agreement with experimental results was found with the mean unsigned errors being less than 1% for the critical temperatures and about 3% (ethers) and 1% (other) for the normal boiling temperatures. For the mixture of acetone + hexane at 328.15 K a positive pressure azeotrope was found with $x_{\text{acetone}}^{\text{azeo}} = 0.71$ in satisfactory agreement with the experimental result of 0.64. Additionally, the structures of hydrogen-bonded aggregates were investigated for 1,2-ethanediol and 2-methoxy-ethan-1-ol, where the average hydrogen bond energies were found to be about -20 and -14 kJ mol $^{-1}$ for inter- and intramolecular hydrogen bonds, respectively.