

# Transferable Potentials for Phase Equilibria.

## 8. United-Atom Description for Thiols, Sulfides, Disulfides and Thiophene

Nusrat Lubna,<sup>†</sup> Ganesh Kamath,<sup>†</sup> Jeffrey J. Potoff,<sup>†,\*</sup> Neeraj Rai,<sup>‡</sup> and J. Ilja Siepmann<sup>‡</sup>

*Department of Chemical Engineering and Materials Science,  
Wayne State University, 5050 Anthony Wayne Drive, Detroit, MI 48202  
Departments of Chemistry and of Chemical Engineering and Materials Science,  
University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455-0431*

### Abstract

An extension of the transferable potentials for phase equilibria united-atom (TraPPE-UA) force field to thiol, sulfide and disulfide functionalities and thiophene is presented. In the TraPPE-UA force field, non-bonded interactions are governed a Lennard-Jones plus fixed point charge functional form. Partial charges are determined through a CHELPG analysis of electrostatic potential energy surfaces derived from ab initio calculations at the HF/6-31g+(d,p) level. The Lennard-Jones well depth and size parameters for four new interactions sites, S (thiols), S(sulfides) S(disulfides), and S(thiophene) were determined by fitting simulation data to pure component vapor-equilibrium data for methanethiol, dimethylsulfide, dimethyldisulfide, and thiophene, respectively. Configurational-bias Monte Carlo simulations in the grand canonical ensemble, combined with histogram-reweighting methods were used to calculate the vapor-liquid coexistence curves for methanethiol, ethanethiol, 2-methyl-1-propanethiol, 2-methyl-2-propanethiol, 2-butanethiol, pentanethiol, octanethiol, dimethylsulfide, diethylsulfide, ethylmethylsulfide, dimethyldisulfide, diethyldisulfide, and thiophene. Excellent agreement with experiment is achieved, with unsigned errors of less than 1% for saturated liquid densities and less than 3% for critical temperatures. Normal boiling points were predicted to within 1% of experiment in most cases, although for certain molecules (pentanethiol) deviations as large as 5% were found. Additional calculations were performed to determine the pressure–composition behavior of ethanethiol+*n*-butane at 373.15 K and the temperature–composition behavior of 1-propanethiol+*n*-hexane at 1.01 bar. In each case, a good reproduction of experimental vapor-liquid equilibrium separation factors is achieved, both the coexistence curves are somewhat shifted due to overprediction of the pure component vapor pressures.

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<sup>†</sup>Wayne State University

<sup>‡</sup>University of Minnesota