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### **Monte Carlo Study of the Thermodynamic and Structural Properties of 1-Butanethiol N-Heptane Mixtures**

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# MONTE CARLO STUDY OF THE THERMODYNAMIC AND STRUCTURAL PROPERTIES OF 1-BUTANETHIOL + N-HEPTANE MIXTURES

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The ability to use computer simulations to predict mixture properties using potential models that have been optimized for the pure compounds is demonstrated. Since the potential models were optimized only for the pure compounds, there is no guarantee that they will describe the interactions between dissimilar molecules in the mixture correctly. In this study, Monte Carlo simulations have been carried out in the isothermal-isobaric (NPT) ensemble to calculate the density and excess enthalpy for 1-butanethiol + n-heptane mixtures at 298.15 K and 1 atm. The OPLS potential-parameters developed by Jorgensen were used to describe the n-heptane molecule. Two models for the butanethiol molecule were employed: PES1 used the OPLS potential-parameters unaltered, while PES2 used the OPLS parameters with slightly modified partial charges. Simulations were performed on mixtures with butyl mercaptan mole fractions of 0.0, 0.23, 0.42, 0.62, 0.83, and 1.0. The average rms deviation between the calculated densities for PES1 and PES2 and the experimental results is 0.021 g/cc and 0.015 g/cc, respectively, while the average rms deviation for the excess enthalpies for PES1 and PES2 is 0.058 kcal/mol and 0.027 kcal/mol, respectively. We also compared our calculated densities with the COSTALD correlation. The extent of self-association of the butanethiol molecules was found to be small for all of the mixtures for the PES2 model.

**KEY WORDS:** Monte Carlo simulations, butanethiol, heptane, mixture, thermodynamic properties.

## 1 INTRODUCTION

Molecular simulations use potential models which are fit to reproduce experimental data, usually for the pure components. Since the parameters are optimized only for the pure compounds, there is no guarantee that they will describe the interactions between dissimilar molecules in the mixtures correctly. For systems with strong interactions, such as mixtures of polar and non-polar components, self-association can occur which results in non-random mixing, and thus these systems can show large deviation from the ideal solution law [1]. Recent studies on strongly interacting systems, i.e., methanol-water mixtures [2–4] and methanol-benzene [5, 6], have shown that molecular simulations can predict mixture properties in good agreement with experiment. These studies employed simple potential models which were optimized to reproduce thermodynamic data for pure methanol and water. In spite of the large number of simulations of liquids, there seem to be no studies on mixtures of thiol-hydrocarbons.

Sulfur compounds, and their behavior with hydrocarbons, are important in the petroleum and chemical industry. The ability to accurately predict the thermodynamic properties of mixtures is critical for the development of practical models which are used

to design and optimize processes for purification, separation, and environmental issues. In particular, thiols (mercaptans) are an important class of compounds used as odorants in the storage of natural gas [7–11]. In an earlier paper [12], we studied the thermodynamic properties of methyl mercaptan and ethyl mercaptan in propane and showed that nonideal behavior was present even at low concentrations of the mercaptan. Unfortunately, we knew of no experimental data for these systems with which to compare our results. Experimental data on the 1-butanethiol/n-heptane mixture were available and used in the present study. In this study, we use potential-energy parameters, which were optimized to reproduce thermodynamic properties of pure 1-butanethiol and n-heptane, and carry out Monte Carlo simulations to calculate the thermodynamic properties and liquid structure in 1-butanethiol + n-heptane mixtures. We compare our simulated thermodynamic results with experimental results [13, 14] and the COSTALD [15, 16] correlation.

## COMPUTATIONAL METHODS

### Potential Energy Surface

The 1-butanethiol (nbSH) and n-heptane molecules were modeled as rigid molecules in their equilibrium configurations [17, 18] and the united atom representation was employed, that is, all  $\text{CH}_3$  and  $\text{CH}_2$  moieties were represented as single sites. Thus, nbSH consists of 6 sites, one centered on each of the four  $\text{CH}_n$  groups, one on the sulfur atom, and one on the hydrogen atom. N-heptane is modeled with seven sites, one on each  $\text{CH}_n$  group. Table 1 lists the geometric parameters used for the nbSH and heptane models.

Since the molecules are held rigid, the total potential-energy surface is given by summing all intermolecular interactions between each site  $i$  on molecule  $k$  and site  $j$  on molecule  $l$  according to

$$u_{kl} = \sum_i \sum_j^{onk onl} \frac{q_i q_j e^2}{r_{ij}} + 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (1)$$

where  $r_{ij}$  is the distance between site  $i$  and site  $j$  and  $\epsilon_{ij}$  and  $\sigma_{ij}$  are obtained using standard combining rules given by

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad (2)$$

and

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j). \quad (3)$$

**Table 1** Geometric Parameters for 1-Butanethiol and n-Heptane

Bonds	$r (\text{\AA})$	Angles	$\theta (\text{deg})$	Dihedral	$\tau (\text{deg})$
C–C	1.53	C–C–C	112.0	C–C–C–C	180.0
C–S	1.82	C–C–S	114.4	C–C–C–S	180.0
S–H	1.34	C–S–H	96.0	C–C–S–H	60.0

The OPLS potential-energy parameters for liquid hydrocarbons [18] were used to model the n-heptane molecule. Two potential-energy surfaces for nbSH were employed in this study. The first potential-energy surface (PES1) used the  $q$ ,  $\epsilon$ , and  $\sigma$  parameters from the set of OPLS parameters for liquid thiols [17] unaltered. Using PES1, we predict a density for pure nbSH of  $0.851 \pm .007$  (g/cc), which is 1.7% higher than the experimental density. The OPLS parameters for the  $-\text{CH}_n-\text{S}-\text{H}$  sites were optimized for smaller thiols (methanethiol and ethanethiol). The second potential-energy surface (PES2) used the  $\epsilon$ , and  $\sigma$  parameters for nbSH from PES1, but scaled the charges ( $q$ ) slightly to give the correct experimental density for pure nbSH [13] at 298 K and 1 atm. The charge parameters were modified since they are independent of the heptane model, whereas the  $\epsilon$ , and  $\sigma$  parameters for all of the  $\text{CH}_n$  sites for nbSH and n-heptane are common. The calculated density and heat of vaporization for the pure components using our modified OPLS model (PES2) are in good agreement with literature values (see below).

Component	$\rho$ (g/cc)		$H_{\text{vap}}$ (kcal/mol)	
	Exp <sup>a</sup>	Calculated	DIPPR <sup>b</sup>	Calculated
Butanethiol	0.83650	$0.834 \pm .006$	8.72	$8.19 \pm .07$
n-Heptane	0.67948	$0.694 \pm .003$	8.69	$9.48 \pm .05$

<sup>a</sup> Reference [13]. <sup>b</sup> Reference [19].

The relationship to the heat of vaporization [17] is shown in Equation 4,

$$\Delta H_{\text{vap}} = E_{\text{intra}}^g - (E_{\text{intra}}^l + E_{\text{inter}}^l) + P\Delta V \quad (4)$$

where  $E_{\text{intra}}$  is the intramolecular energy which is neglected since the molecules are held rigid and  $E_{\text{inter}}$  is the intermolecular energy for the liquid.  $P\Delta V$  is essentially  $RT$  [2, 20], where  $R$  and  $T$  are the gas constant and the temperature. The potential-energy parameters for both PES1 and PES2 are listed in Table 2. The factor  $e^2$  in Equation (1) is 332.18 kcal Å/mol.

Intermolecular interactions were truncated according to a spherical cut-off based on the center-of-mass distance between molecules. The cut-off value was a little less than half the box length. Corrections to the potential energy arising from truncations of intermolecular interactions were calculated according to

$$E_{\text{cut}} = 2\pi N \sum_k \sum_l \sum_i \sum_j \int_{r_c}^{\infty} \chi_k \rho_l r_{ij}^2 g_{ij}(r) u_{ij}(r) dr, \quad (5)$$

where  $M$  is the number of different components in the solution,  $x_k = N_k/N$ ,  $\rho_l = N_l/V$ , where  $N$  is the total number of molecules ( $N = N_1 + N_2 + \dots + N_M$ ),  $V$  is the volume of the cube,  $r_{ij}$  is the radial distance between sites  $i$  and  $j$ ,  $g_{ij}$  is the radial distribution function between sites  $i$  and  $j$  (assumed to be unity beyond the cutoff distance  $r_c$ ), and

**Table 2** Site<sup>a</sup> parameters for 1-Butanethiol and n-Heptane

site	$q^b$		$\epsilon$ (kcal/mol)	$\sigma$ (Å)
	PES1	PES2		
CH <sub>3</sub> (in n-heptane)	0.00	0.00	0.175	3.905
CH <sub>2</sub> (in n-heptane)	0.00	0.00	0.118	3.905
CH <sub>3</sub> (in butanethiol)	0.00	0.00	0.175	3.905
CH <sub>2</sub> (in butanethiol)	0.00	0.00	0.118	3.905
CH <sub>2</sub> -S (in butanethiol)	0.18	0.16	0.118	3.905
S	-0.45	-0.39	0.250	3.550
H	0.27	0.23	0.000	0.000

<sup>a</sup> CH<sub>n</sub> groups are modeled as single sites.<sup>b</sup> Units are electrons.

$u_{ij}$  is the intermolecular pairwise interaction between sites  $i$  and  $j$ . A correction was not made for the truncated electrostatic interaction [2, 17, 21, 22].

### Monte Carlo Procedure

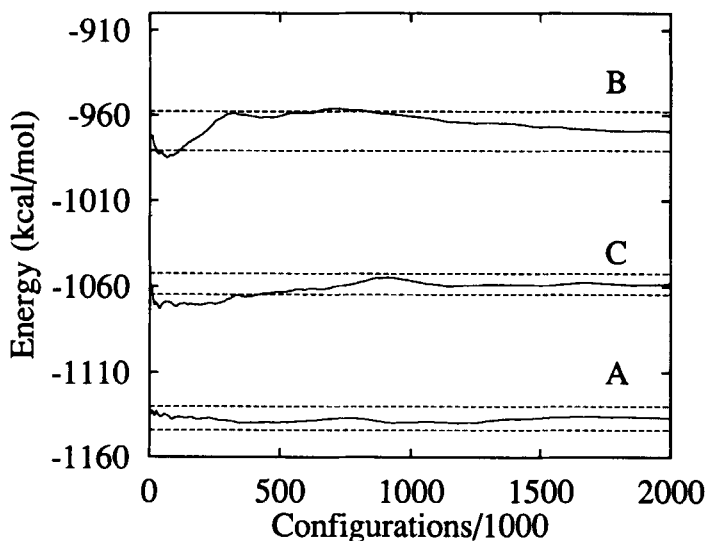
The Monte Carlo (MC) calculations were carried out using standard procedures including periodic boundary conditions, Metropolis sampling [23], and the isothermal-isobaric (NPT) ensemble [24]. The total number of molecules remained fixed at 128. The initial density was taken as the final density from each previous run. We studied six solutions where the mole fraction of nbSH was 0.0, 0.23, 0.42, 0.62, 0.83 and 1.0. The temperature and external pressure were fixed at 298.15 K and 1 atm, respectively. New configuration were generated by randomly selecting a molecule, translating it randomly in all three Cartesian directions, and randomly rotating it about a randomly chosen axis. A volume move was attempted every 1000 configurations, and all the intermolecular distances were scaled accordingly. The ranges were chosen to yield an acceptance ratio of about 0.45 for new configurations.

The initial configuration of each solution was a random distribution of the mercaptan and alkane molecules on a cubic lattice. The volume of the cube was determined by the initial density and number of molecules. Each simulations had an equilibration period of  $1 \times 10^6$  configurations which was discarded. Averages of the computed properties were obtained over an additional  $2.0 \times 10^6$  configurations. The statistical uncertainties ( $\pm 1\sigma$ ) reported were obtained from averages over 5 subsets of each simulation. A sequence of  $1 \times 10^6$  steps took approximately 6 hr. of CPU time on an IBM RISC/6000 model 590 workstation.

## RESULTS AND DISCUSSION

### Thermodynamics

Figure 1(a-c) illustrates the convergence of the average total energy for three different solutions; pure n-heptane, pure nbSH, and a mixture with a mole fraction of nbSH of



**Figure 1** Average total energy versus configurations for: A) pure heptane; B) pure 1-butanethiol; and C) a 0.42 mole fraction of 1-butanethiol mixture. The solid lines represent the cumulative averages and the standard deviations are the dashed lines.

0.42. The larger fluctuations initially are due to the smaller number of data comprising the average. It can be seen that the total energy for n-heptane (see Figure 1a) and nbSH (see Figure 1b) is well equilibrated after  $1.0 \times 10^6$  steps. The mixture (see Figure 1c) is not fully equilibrated after  $1.0 \times 10^6$  steps, but required about 400 K more steps before the average energy remained inside the  $1\sigma$  standard deviation.

The calculated densities using both PES1 and PES2 for pure nbSH, n-heptane, and four nbSH/n-heptane mixtures at 298.15 K and 1 atm. are listed in Table 3 and are shown in Figure 2. Good agreement with experimental data is obtained using these models. The average root-mean-square (rms) deviation between our calculated densities and the experimental results for PES1 and PES2 are 0.021 g/cc and 0.015 g/cc,

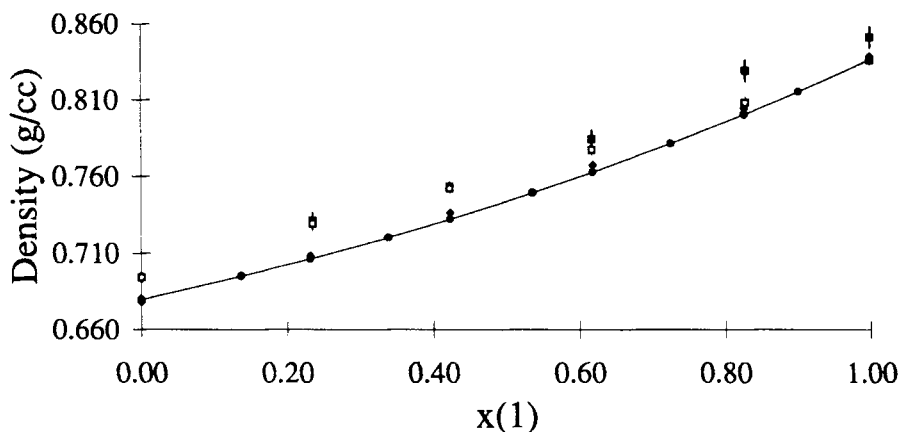
**Table 3** Densities for 1-Butanethiol(1) + n-Heptane(2) Mixtures.<sup>a</sup>

<i>x</i> (1)	<i>ρ</i> (g/cc)			
	<i>Exp</i> <sup>b</sup>	<i>PES1</i>	<i>PES2</i>	<i>COSTALD</i> <sup>c</sup>
0.00	0.67948	0.694 ± .003	0.694 ± .003	0.6782
0.23	0.70608	0.731 ± .005	0.729 ± .005	0.7084
0.42	0.73208	0.753 ± .003	0.752 ± .003	0.7361
0.62	0.76249	0.784 ± .006	0.777 ± .004	0.7673
0.83	0.80020	0.829 ± .007	0.808 ± .004	0.8043
1.00	0.83650	0.851 ± .007	0.834 ± .006	0.8385

<sup>a</sup> Temperature and pressure are 298.15 K and 1 atm.

<sup>b</sup> Reference [13]. Standard deviation is 0.00002.

<sup>c</sup> Reference [15, 16].



**Figure 2** Densities for 1-butanethiol + n-heptane mixtures as a function of the mole fraction  $x$  of 1-butanethiol: ●, experiment; ◆, COSTALD; ■, PES1 from this work; □, PES2 from this work.

respectively. For PES1, the density is consistently high for all of the mixtures studied (see Figure 2). For PES2, the largest deviations between the calculated and experimental densities occur in the n-heptane-rich region and is due to the inaccuracy of the n-heptane parameters. The density for pure n-heptane is 2.1% too large compared with experiment. These results are surprisingly good, since the OPLS parameters only used linear alkanes up to n-butane in the fitting procedure for all n-alkanes [18]. Therefore, optimizing the parameters for n-heptane would most likely increase the agreement between experiment and simulation over the concentration range, but this is beyond the scope of this study. We also predicted the densities for the six solutions using the COSTALD correlation [15,16] and the results are given in Table 3 and shown in Figure 2. The average rms deviation between the densities predicted using COSTALD and the experimental results is 0.003 g/cc. The results for the densities (Figure 2) show that our model does not predict a large enough volume expansion for these mixtures compared with experiment, while the COSTALD correlation is in much better agreement. Decreasing the self-interaction between n-heptane molecules ( $\epsilon$  parameter) or increasing the molecular volume of the n-heptane molecules ( $\sigma$  parameter) would bring the density in the heptane-rich regions into better agreement with experiment.

The excess volume ( $V^E$ )

$$V_{12}^E = V_{12} - (x_1 V_1^0 + x_2 V_2^0) \quad (6)$$

can be obtained from the density  $\rho$  of each mixture according to the relation

$$V_{12}^E = (x_1 M_1 + x_2 M_2) / \rho_{12} - (x_1 M_1 / \rho_1 + x_2 M_2 / \rho_2) \quad (7)$$

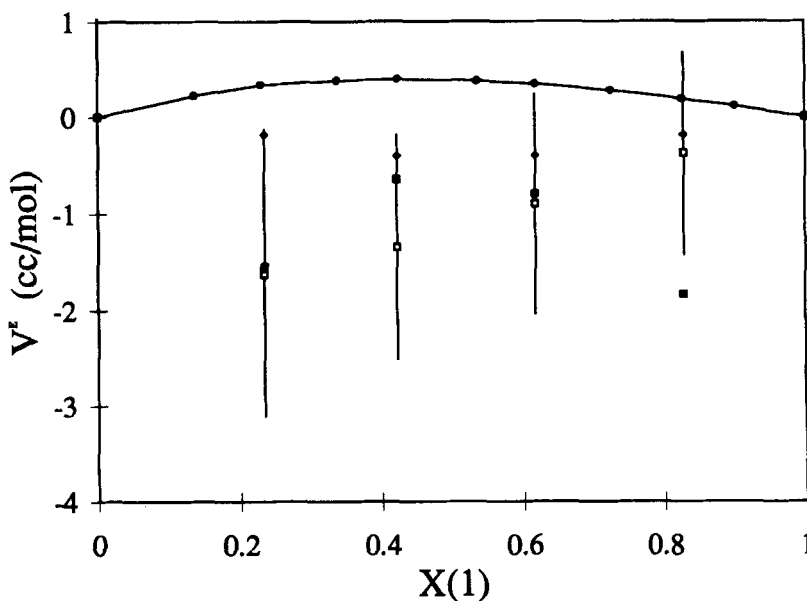
where  $V_{12}$  is the molar volume of the mixture at composition  $x_1$  ( $x_2 = 1 - x_1$ ) and  $V^0$  is the average volume of the pure component. In Equation (7),  $M_i$  is the molecular weight and  $\rho_i$  is the density of pure component  $i$ . The calculated excess volumes obtained from the simulations, COSTALD correlation, and experimental data are given in Table 4 and are illustrated in Figure 3. As can be seen from Figure 3, both the COSTALD

**Table 4** Excess volumes  $V^E$  for 1-Butanethiol(1) + n-Heptane(2) Mixtures.<sup>a</sup>

$x(1)$	$V^E(\text{cc/mol})$			
	$Exp^b$	$PES1$	$PES2$	$COSTALD^c$
0.23	0.334	$-1.5 \pm 1.7$	$-1.6 \pm 1.5$	-0.186
0.42	0.394	$-0.7 \pm 1.3$	$-1.4 \pm 1.1$	-0.401
0.62	0.345	$-0.8 \pm 1.7$	$-0.8 \pm 1.1$	-0.397
0.83	0.186	$-1.7 \pm 1.8$	$-0.4 \pm 1.0$	-0.185

<sup>a</sup> Temperature and pressure are 298.15 K and 1 atm.<sup>b</sup> Reference [13]. Standard deviation is 0.004.<sup>c</sup> Reference [15, 16].

correlations and the simulation results predict a negative excess volume whereas, the experimental results show a positive excess volume. The excess volume is a very sensitive measure and small deviations in the density result in large deviations in the excess volume. The average rms deviation in the COSTALD densities is 0.003 g/cc, yet the COSTALD correlation predicts an excess volume at  $x_1 = 0.42$  that is low by about 200%. Therefore, due to the large discrepancies between the experimental and simulation densities (see Figure 2), quantitative comparison between the excess volumes obtained from experimental data and simulations is not practical.

**Figure 3** Excess Volumes  $V^E$  of 1-butanol + n-heptane mixtures at 298.15 K as a function of the mole fraction  $x$  of 1-butanol: ●, experiment; ◆, COSTALD; ■, PES1 from this work; □, PES2 from this. The error bars are for PES2 only.

The excess enthalpy ( $H^E$ ), given by

$$H_{12}^E = H_{12} - (x_1 H_1^0 + x_2 H_2^0) \quad (8)$$

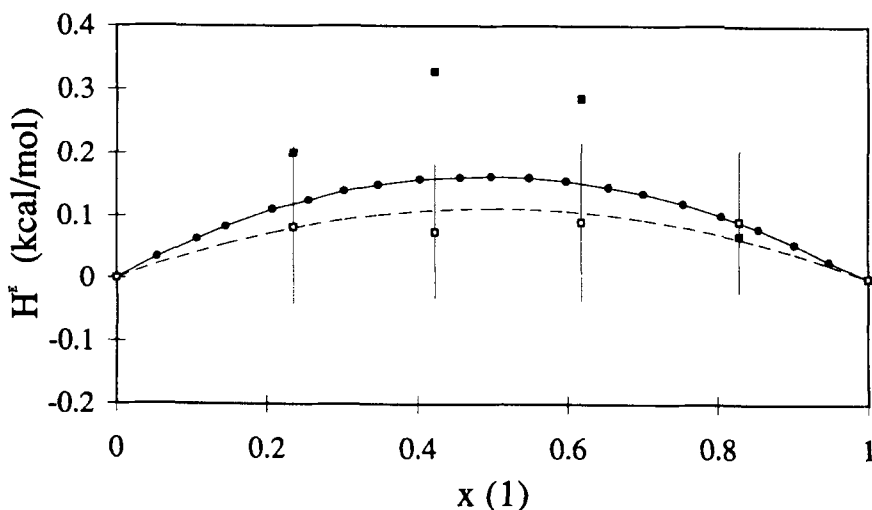
where  $H_{12}$  is the average energy of the mixture and  $H^0$  is the average energy of the pure component, was calculated for the four different nbSH(1)-heptane(2) mixtures using both PES1 and PES2. The pv term was ignored in the enthalpy calculations. The calculated and experimental [14]  $H^E$ s are given in Table 5 and are illustrated in Figure 4. The experimental values lie within the statistical error associated with the simulation results. The simulation results give the correct qualitative behavior in the excess enthalpy, but due to the large statistical uncertainty, definitive conclusions are unwarranted. The average rms deviations between the calculated and experimental  $H^E$  for PES1 and PES2 are 0.058 kcal/mol and 0.023 kcal/mol, respectively. The dashed line is a best fit to the simulated data for PES2. For PES2, the large deviation at nbSH

**Table 5** Excess enthalpies  $H^E$  for 1-Butanethiol(1) + n-Heptane (2) Mixtures.<sup>a</sup>

$x(1)$	$H^E$ (kcal/mol)		
	<i>Exp</i> <sup>b</sup>	<i>PES1</i>	<i>PES2</i>
0.23	0.1245	$0.20 \pm 1.8$	$0.08 \pm .12$
0.42	0.1617	$0.33 \pm .16$	$0.07 \pm .11$
0.62	0.1558	$0.29 \pm .19$	$0.09 \pm .12$
0.83	0.1011	$0.07 \pm .25$	$0.09 \pm .11$

<sup>a</sup> Temperature and pressure are 298.15 K and 1 atm.

<sup>b</sup> Reference [14].



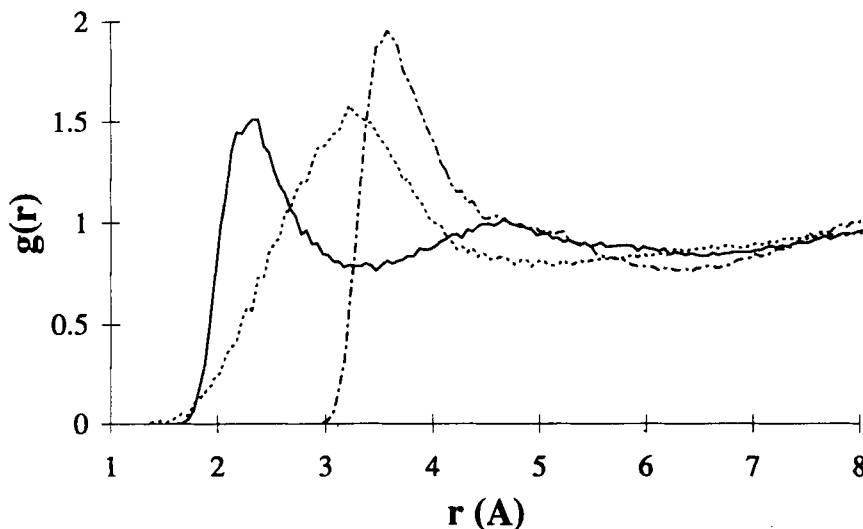
**Figure 4** Excess Enthalpies  $H^E$  of 1-butanol + n-heptane mixtures at 298.15 K as a function of the mole fraction  $x$  of 1-butanol: ●, experiment; ■, PES1 from this work; □, PES2 from this work; ---, best fit to the simulated data. The error bars are for PES2 only.

mole fraction  $x_1 = 0.42$  in the excess enthalpy (see Figure 4) is probably due to the discrepancy in the OPLS parameters for pure n-heptane. Smaller  $\epsilon$  parameters for n-heptane would decrease the self-interaction between heptane molecules and therefore, would lower the enthalpy for pure n-heptane ( $H_2^0$ ). But a decrease in the  $\epsilon$  parameters would also result in a decrease in the cross-interaction between nbSH and heptane molecules and therefore decrease the enthalpy of mixing ( $H_{12}$ ). In the heptane-rich regions, the change in the  $H_2^0$  term for heptane (fourth term in Equation 8) should be larger than the change in the  $H_{12}$  term for nbSH + heptane mixtures (second term in Equation 8) since in this region, there are fewer nbSH-heptane interactions while the  $H_2^0$  term is large. The net results should be an increase in the excess enthalpy in the heptane-rich region. The  $H_1^0$  term for nbSH (third term in Equation 8) would be unaffected by the changes in the heptane parameters.

### Radial Distribution Functions

Solvent structure can be obtained from the atom-atom radial distribution functions,  $g_{xy}(r)$ , which represent the probability of occurrence of atoms of type  $y$  at a distance  $r$  from atoms of type  $x$  [24]. The liquid structure results of only PES2 are discussed here. The calculated radial distribution functions (rdfs) for S-S, S-H, and H-H atom pairs for pure nbSH are shown in Figure 3. The rdfs for the mixtures show the same structure as that for pure nbSH. The first peak in the S-S and S-H rdf confirms self-association is present. The number of nearest neighbors is obtained by integrating  $g_{xy}(r)$  to the first minimum.

The number of thiol-thiol nearest neighbors for the different solutions studied are given in Table 6. For pure nbSH, the results are consistent with the nbSH molecule



**Figure 5** Atom-Atom Radial Distribution Function for pure 1-butanethiol:—, S-H; ---, H-H; — · — · —, S-S.

**Table 6** Radial distribution Function Analysis for 1-Butanethiol.

[Mol% nbSH]	<i>S-S</i> <sup>a</sup>	<i>S-H</i> <sup>b</sup>	<i>H-H</i> <sup>a</sup>
23	0.44	0.15	0.51
42	0.98	0.33	1.08
62	1.32	0.41	1.49
83	1.63	0.48	1.81
100	1.94	0.57	2.19

<sup>a</sup> Integration to the first minimum at 4.5 (Å).<sup>b</sup> Integration to the first minimum at 3.05 (Å).

participating in approximately 0.57 hydrogen bonds. As the nbSH concentration decrease, the number of hydrogen bonds per mercaptan molecule decreases to 0.15. The results show that the extent of self-association for this system is small. These results are in agreement with experimental results which show some hydrogen bonding exists in nbSH solutions [14]. This is in contrast with our earlier study on methanethiol/propane and ethanethiol/propane mixtures [12], which showed the mercaptan molecules participating in approximately 1.0 hydrogen bond for the pure mercaptan solutions and decreasing to about 0.6 hydrogen bonds as the mercaptan mole fraction decreased to 0.06. These results are reasonable since the hydrogen bonding should decrease as the alkane chain increases due to steric effects.

## CONCLUSIONS

Our results show that potential models, optimized for the pure components, can adequately describe the mixture properties for weakly interacting systems. Two potential-energy surfaces were used. For PES1, the OPLS potential parameters for n-heptane and butyl mercaptan were used unaltered, while for PES2, the potential parameters for butyl mercaptan were slightly modified from the literature values to give better pure component properties. For predicting the density of these mixtures, molecular simulations and the COSTALD correlations are in very good agreement with experimental data. The average rms deviation between the calculated densities and the experimental results are 0.021 g/cc and 0.015 g/cc for PES1 and PES2, respectively. The excess volumes from both the COSTALD correlation and simulation predict a negative excess volume while the experimental results yield a positive  $V^E$ . The average rms deviation between the calculated  $H^E$ 's and the experimental results are 0.058 kcal/mol and 0.027 kcal/mol for PES1 and PES2, respectively. The small  $H^E$ 's show that this system is a very weakly interacting mixture and therefore, the nonideal behavior is very small. But due to the large statistical uncertainty, quantitative conclusions are unwarranted. Self-association is shown to be small even for pure butyl mercaptan. The self-association decreases with decreasing butyl mercaptan concentration. The small nonideal behavior makes this system a very stringent test for obtaining quantitative agreement between our molecular simulations and experimental data, and therefore, the good agreement is promising.

### Acknowledgment

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