

# The Use of Molecular Orbital Calculations to Describe the Phase Behavior of Hydrogen-Bonding Mixtures<sup>1</sup>

J. P. Wolbach<sup>2</sup> and S. I. Sandler<sup>2,3</sup>

---

In previous studies we have used Hartree-Fock theory and density functional theory to compute the enthalpy and entropy changes of dimerization for methanol and a number of small carboxylic acids. We have shown that by using these results in a physical equation of state, the statistical associating fluid theory (SAFT), we are able to model the phase behavior of these pure hydrogen-bonding compounds with a reduction in the number of adjustable parameters; in this study, we use the pure-component parameters derived from the results of our molecular orbital calculations to describe the phase behavior of mixtures containing one associating and one nonassociating compound, again using the SAFT equation of state. We show that the use of the pure-component SAFT parameters derived from our quantum-mechanical calculations results in correlations of mixture VLE data with no loss of accuracy, and frequently with improved accuracy, compared to the original parameters reported for use with the SAFT model.

---

**KEY WORDS:** associating mixtures; hydrogen bonding; molecular orbital calculations.

## 1. INTRODUCTION

Molecular association has an important effect on the phase behavior of pure fluids and mixtures. As a result, much effort has been expended on modeling the effects of association. These efforts can be separated into two classes: chemical theories, which postulate the formation of distinct molecular aggregates in solution, and physical theories, which model the

---

<sup>1</sup> Paper dedicated to Professor Edward A. Mason.

<sup>2</sup> Center for Molecular and Engineering Thermodynamics, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716, U.S.A.

<sup>3</sup> To whom correspondence should be addressed.

association as being the result of a strong, specific molecular interaction. Both methods suffer from the use of a large number of ill-defined adjustable parameters in order to obtain good fits of experimental phase behavior data. If one were able to determine these association parameters *a priori*, such methods would be more useful, and possibly even completely predictive.

In previous studies we used *ab initio* molecular orbital calculations to determine the thermodynamic parameters of association for pure hydrogen-bonded dimers of small organic compounds, and have compared the results of our calculations to experimental estimates of the thermodynamic parameters where they are available [1, 2]. We have then used our calculated parameters in a physical equation of state, the statistical associating fluid theory (SAFT), and showed that using the information obtained from the molecular orbital calculations allows a reduction in the number of adjustable parameters in the SAFT equation of state for pure associating compounds with little or no loss in accuracy.

In this study, we apply the results of our molecular orbital calculations to binary mixtures of an associating compound and a diluent. We again use the SAFT equation and consider mixtures containing methanol or a small carboxylic acid (formic, acetic, or propionic) as the associating component. We show that the pure-component parameters derived from the results of our molecular orbital calculations may be used to correlate mixture data with fewer adjustable parameters and better accuracy than in the original SAFT model.

## 2. MOLECULAR ORBITAL CALCULATIONS

We have performed *ab initio* molecular orbital calculations to determine the enthalpy, entropy, Gibbs free energy, and heat capacity changes for a number of hydrogen-bonding dimerization "reactions." These calculations are for the association of isolated pairs of molecules and are representative of vapor-phase dimerization. The calculations were performed using two calculational methods: the computationally inexpensive Hartree-Fock (H-F) method and the more rigorous density functional theory (DFT) method. The H-F calculations were performed using the small 6-31g(d, p) basis set, while the DFT calculations were performed using the Becke3LYP functional and the medium-sized 6-31++ g(2d, p) basis set. Details of these calculations and a discussion of these two calculational methods were presented earlier [1].

We present the results of our calculations for the associating compounds considered in this study in Table I. The methanol dimer is linear, while the carboxylic acid dimers are cyclic, as these compounds have been experimentally observed to form only such dimers in the vapor phase. Pre-

Table 1. Results of Molecular Orbital Calculations for Pure Dimers<sup>a</sup>

	H-F			DFT			
	$\Delta H$ (kcal·mol <sup>-1</sup> )	$\Delta S$ (cal·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta C_p^{\ddagger}$ (cal·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta H$ (kcal·mol <sup>-1</sup> )	$\Delta S$ (cal·mol <sup>-1</sup> ·K <sup>-1</sup> )	$\Delta C_p^{\ddagger}$ (cal·mol <sup>-1</sup> ·K <sup>-1</sup> )	$K_{eq}$ $2.53 \times 10^{-3}$
Methanol	-3.877	-19.937	3.07	-3.130	-22.379	2.75	2.53 × 10 <sup>-3</sup>
Formic acid	-13.557	-34.515	2.22	-13.497	-37.290	1.39	55.5
Acetic acid	-13.924	-34.052	2.26	-13.958	-36.097	1.46	220
Propionic acid	-13.720	-34.311	2.27	-13.742	-37.205	1.50	87.5

<sup>a</sup> All thermodynamic quantities calculated at 298.15 K and 1 atm.

72

viously [2] we have shown that both calculational methods led to results which were found to be in agreement with the available experimental estimates. Although the results for the methanol dimer are quite different for the two calculational methods, there are large discrepancies in the reported experimental estimates for these types of weakly associating compounds.

### 3. USE OF CALCULATED THERMODYNAMIC QUANTITIES

#### 3.1. Application to Pure Components

We initially used our calculated results in an equation-of-state model to describe the phase behavior of pure associating compounds. The equation of state we chose is the statistical associating fluid theory (SAFT) developed by Chapman and co-workers [3-5] from the first-order thermodynamic perturbation theory (TPT1) of Wertheim [6-9]. SAFT has been shown to yield accurate correlations for the properties of associating and nonassociating fluids over a wide range of molecular sizes [10-12].

In this model pure fluids are treated as chains of equal-sized spherical segments interacting with a square-well potential. The equation of state is expressed in terms of the residual Helmholtz free energy and contains three parameters for nonassociating compounds: the number of segments ( $m$ ), the volume of an individual segment ( $v^{00}$ ), and the depth of the square-well potential ( $u^0/k$ ). In order to describe association, molecules are assigned specific bonding sites, and the interactions between these sites are modeled using the square-well potential. This introduces two additional parameters for pure associating fluids. The well depth of the interaction between association site A and association site B is described by the parameter  $\epsilon^{AB}/k$ , and the well width characterized by the dimensionless parameter  $\kappa^{AB}$ . Further details of the SAFT equation for pure components are presented elsewhere [2].

In an earlier study [13], we reported a procedure by which we related the results of our molecular orbital calculations to the association parameters in SAFT. This was done by forcing the vapor-phase composition of monomers and dimers at low pressures predicted by the SAFT equation to match the composition predicted by our molecular orbital calculations. As a result, we were able to fit pure-component vapor pressure and liquid density data for associating compounds using fewer adjustable parameters than in the original SAFT model. We now summarize our results for the compounds considered in this study.

One of the restrictions of TPT1 is that pairs of molecules may only singly bond, so in order to account for the formation of cyclic dimers in the vapor phase of the carboxylic acids, these are assigned only one bonding

site per molecule. This is the same choice made by Huang and Radosz in the original implementation of SAFT [10].

Our fits to the data for pure formic and acetic acids involved only three adjustable parameters, while our fit to VLE data for propionic acid used only two adjustable parameters. This is an improvement from original SAFT, which used at least four, and possibly five, adjustable parameters. The average errors in calculated vapor pressure and liquid density from both our methods, along with the errors from using the best-fit parameters of the original SAFT, are presented in Table II. Our best-fit parameters for both the H-F and the DFT calculational methods are presented in Table III.

Methanol contains one hydrogen-bonding proton and two lone electron pairs. If one includes all of these as potential bonding sites, methanol would be assigned three association sites. Alternatively, one could postulate that it is not possible to bond to both lone electron pairs simultaneously and then treat methanol as having only two association sites.

We tested both models when fitting the pure-component data, using only three adjustable parameters in each case. For comparison, in the original SAFT model methanol was assumed to have two association sites, and four adjustable parameters were used. We found that our best fit when using H-F-based parameters was obtained with a three-site association model. However, we were unable to obtain a fit of the vapor pressure with average errors of less than 5% using our DFT results with either association model. Consequently, we used the three-site model with the H-F

Table II. Average Errors for the Associating Compounds in this Study<sup>a</sup>

Compound	Model	No. of sites	T range (K)	% error $P^{vap}$	% error $\rho^{liq}$
Formic acid	Original SAFT	1	293–393	0.62	0.49
	H-F	1		0.76	0.27
	DFT	1		0.62	0.10
Acetic acid	Original SAFT	1	283–573	1.90	0.65
	H-F	1		0.86	1.58
	DFT	1		0.94	0.63
Propionic acid	Original SAFT	1	313–463	0.35	0.09
	H-F	1		0.87	0.67
	DFT	1		0.75	0.87
Methanol	Original SAFT	2	257–483	0.83	0.88
	H-F	3		1.23	0.64

<sup>a</sup> Data from *Thermodynamic Tables for Non-Hydrocarbons* (Thermodynamic Research Center Center, Texas A&M University, College Station: loose pages to 1995).

Table III. The Best-Fit Parameters for Species Considered in This Study

Compound	H-F				DFT				
	$r'$ ( $\text{cm}^3 \cdot \text{mol}^{-1}$ )	$m$	$u^0/k$ (K)	$e^{\text{AB}}/k$ (K)	$\kappa^{\text{AB}} \times 10^3$	$r'$ ( $\text{cm}^3 \cdot \text{mol}^{-1}$ )	$u^0/k$ (K)	$e^{\text{AB}}/k$ (K)	$\kappa^{\text{AB}} \times 10^3$
Formic acid	18.20	1.176	369.86	4160	582.3	19.75	1.099	394.33	3771
Acetic acid	18.20	1.684	305.97	5751	3.465	19.75	1.582	321.28	5490
Propionic acid	18.20	2.192	282.51	6123	0.855	19.75	2.065	306.75	5395
Methanol	8.10	2.679	222.57	1930	44.72	—	—	—	—
Diluents									
						Compound	$r'$ ( $\text{cm}^3 \cdot \text{mol}^{-1}$ )	$m$	$u^0/k$ (K)
Formic acid	15.5	1.341	333.28	7522	1.625	<i>n</i> -Pentane	12.533	4.091	200.02
Acetic acid	14.5	2.132	290.73	3941	39.26	<i>n</i> -Heptane	12.282	5.391	204.61
Propionic acid	13.5	3.084	296.03	3400	8.193	Benzene	11.421	3.749	250.19
Methanol	12.0	1.776	216.13	2714	48.56	Chloroform	10.971	3.661	240.31
						Carbon tetrachloride	13.730	3.458	257.46
						1-Chloropropane	11.946	3.600	229.14

results only when correlating mixture data. The average errors in the calculated vapor pressure and liquid density of our three-site H-F fit, along with those of the original SAFT, are presented in Table II. The optimized parameter values for both methods are included in Table III.

### 3.2. Correlation of Mixture Data

To test whether the pure-component SAFT parameters derived from our molecular orbital calculations could improve the correlation of mixture VLE data, we fit low-pressure data for systems containing one associating compound and one diluent (nonassociating compound) using a single binary interaction parameter and the vdW one-fluid mixing rules. The binary interaction parameter enters into the mixing rule for the averaged depth of the square well ( $u/kT$ ),

$$\frac{u}{kT} = \frac{\sum_i \sum_j x_i x_j m_i m_j [u_{ij}/kT] (v^0)_{ij}}{\sum_i \sum_j x_i x_j m_i m_j (v^0)_{ij}} \quad (1)$$

where

$$(v^0)_{ij} = \left[ \frac{1}{2} [(v^0)_i]^3 + (v^0)_j^3 \right]^3 \quad (2)$$

and

$$u_{ij} = (1 - k_{ij})(u_{ii} u_{jj})^{1/2} \quad (3)$$

In Eq. (2), the temperature-dependent segment volume ( $v^0$ ) is related to the temperature-independent segment volume ( $v^{00}$ ) in the following way

$$v^0 = v^{00} \left[ 1 - 0.12 \exp\left(\frac{-3u^0}{kT}\right) \right]^3 \quad (4)$$

while the parameter  $u_{ii}$  (the temperature-dependent square-well depth) in Eq. (3) may be expressed as

$$\frac{u_{ii}}{k} = \frac{u_i^0}{k} \left[ 1 + \frac{e}{kT} \right] \quad (5)$$

In Eq. (5),  $e/k$  is a constant that has been correlated with Pitzer's acentric factor and the critical temperature [14, 15] for various molecules. However, in this work the energy parameter is for segments, not molecules, and a value of 10 for  $e/k$  was assumed for all the compounds studied [10, 16]. This is the same procedure followed by Huang and Radosz [16]

when fitting low-pressure mixture VLE data, and further details on the equation of state for mixtures are given there.

We used the SAFT parameters derived by Huang and Radosz [10] for the diluent in each system, and these parameters are presented in Table III. We performed either bubble-point pressure or bubble-point temperature calculations, depending on whether the data used were obtained at constant temperature or pressure. The objective function minimized when fitting the data was, respectively,

$$z = \sum \frac{|P^{\text{calc}} - P^{\text{exp}}|}{P^{\text{exp}}} + \sum \frac{|y_i^{\text{calc}} - y_i^{\text{exp}}|}{y_i^{\text{exp}}} \quad (6)$$

or

$$z = \sum \frac{|T^{\text{calc}} - T^{\text{exp}}|}{T^{\text{exp}}} + \sum \frac{|y_i^{\text{calc}} - y_i^{\text{exp}}|}{y_i^{\text{exp}}} \quad (7)$$

### 3.2.1 Mixtures Including Acids

We initially considered mixtures of propionic acid and *n*-heptane at two temperatures, and the results are shown in Fig. 1. At both temperatures our parameter sets for the acid produce better results than the original SAFT parameters, although our parameter sets do require somewhat larger values of the binary interaction parameter.

We next considered bubble temperature calculations for mixtures of propionic acid + benzene and propionic acid + carbon tetrachloride. These results are presented in Fig. 2. Again, the parameter sets derived from our quantum mechanical calculations gave excellent agreement with the experimental data, performing better than the original SAFT parameters, though, again, the optimum values of the binary interaction parameter are somewhat larger than those for the original SAFT parameters.

Our binary interaction optimization procedure had to be modified for the acetic acid + *n*-heptane system. At 30°C, this system forms an azeotrope, and the use of Eq. (6) as the objective function in the optimization resulted in values of the binary interaction parameter that led to predictions of liquid–liquid equilibrium, regardless of the parameter set used. Consequently in the optimization we constrained the binary interaction parameter to values which did not allow for liquid–liquid equilibrium. Mathematically, the constraint forces  $(\partial P / \partial x_{\text{acid}})_T$  to change sign only once and  $(\partial y_{\text{acid}} / \partial x_{\text{acid}})_T$  not to change sign. This is the only system in this study for which such a procedure was used. Figure 3 displays the results. The



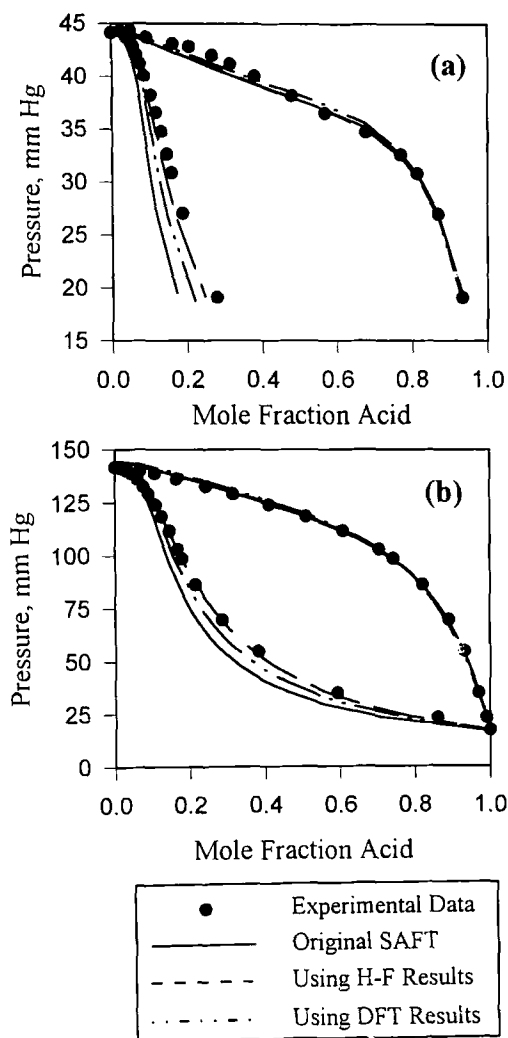


Fig. 1. Bubble pressure calculations for the mixtures propionic acid + *n*-heptane at 25°C (a) and 50°C (b). In (a), the SAFT parameters for *n*-heptane were reoptimized to fit the pure *n*-heptane limit of the system pressure. The new optimum parameters are  $u^0 k = 199.93$ ,  $m = 5.618$ , and  $v^{00} = 12.04$ .

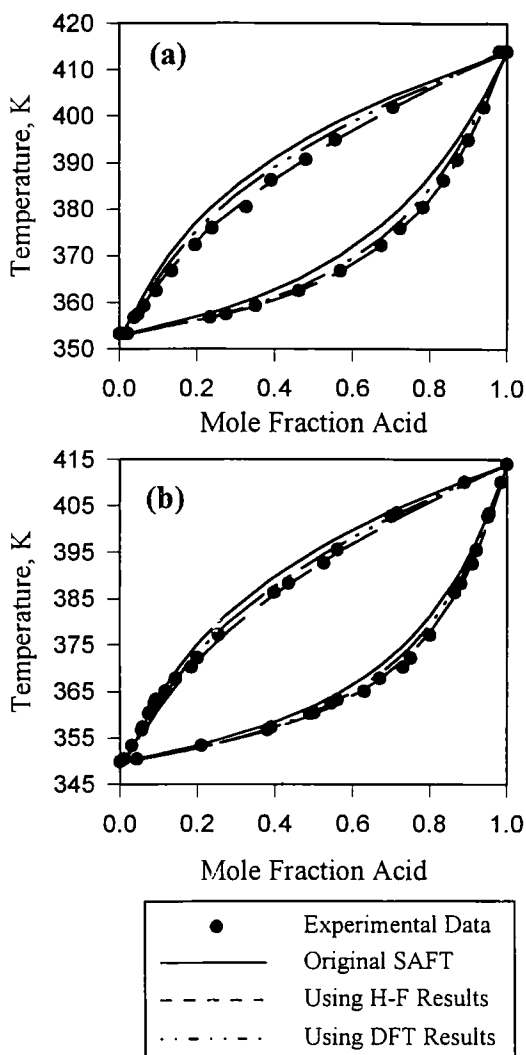


Fig. 2. Bubble temperature calculations for the systems propionic acid + benzene (a) and propionic acid +  $\text{CCl}_4$  (b). Both systems are at a pressure of 760 mm Hg.

parameter sets derived from quantum mechanics are better able to predict the azeotropic and vapor-phase compositions than the parameters of the original SAFT model, although the total pressure is too low for all the models.

Figure 4 contains the results for the acetic acid + benzene and acetic acid + carbon tetrachloride systems, respectively. These systems again show that using parameter sets for the pure acids which have been derived from the molecular orbital calculations results in a better correlation of mixture phase-equilibrium data.

In our fits of mixture phase behavior involving formic acid, we studied one azeotropic system (formic acid + 1-chloropropane) and one system which exhibited liquid-liquid equilibrium (formic acid + benzene). As the three parameter sets performed nearly identically on these systems, we do

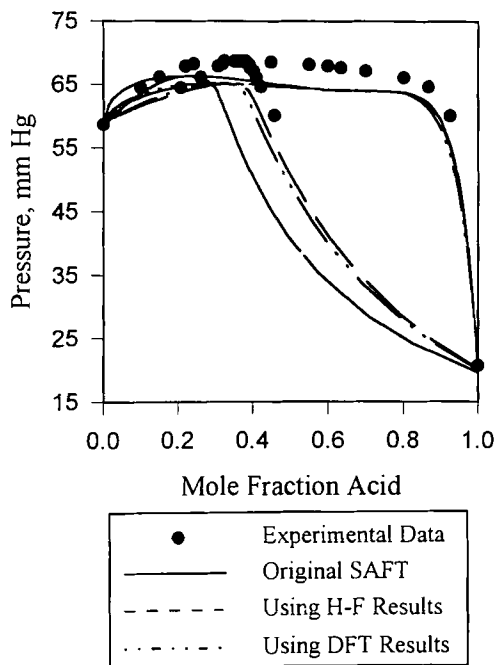


Fig. 3. Bubble pressure calculations for the system acetic acid + *n*-heptane at 30°C. The experimental azeotropic composition is  $x_{\text{acid}} \sim 0.36$ . Using the original SAFT parameters the azeotropic composition is predicted to be  $x_{\text{acid}} \sim 0.225$ , while use of the parameters derived from either set of our quantum mechanical results produces an azeotrope at  $x_{\text{acid}} \sim 0.325$ .

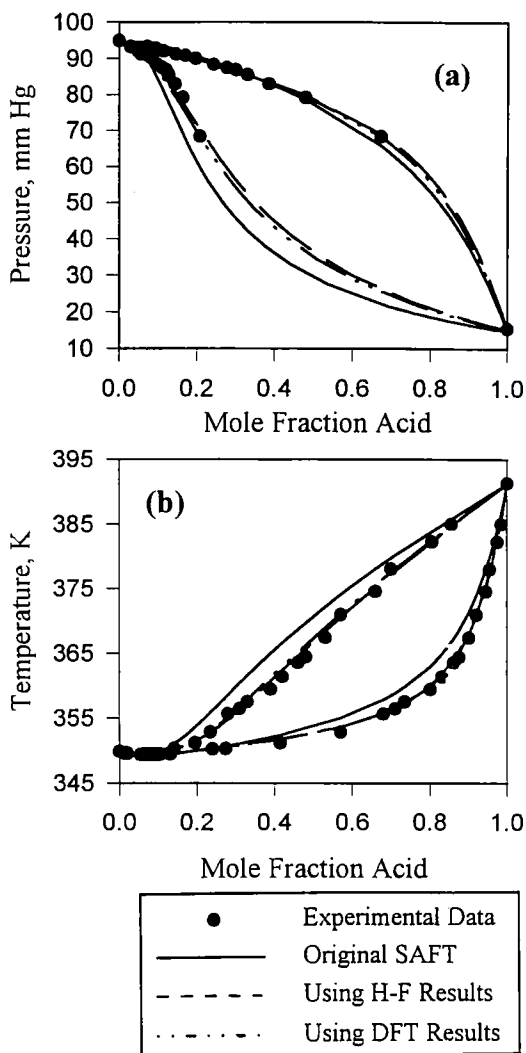


Fig. 4. Bubble pressure calculations for the system acetic acid + benzene at 25°C (a) and bubble temperature calculations for the system acetic acid +  $\text{CCl}_4$  at 460 mm Hg (b). In b, the two lines corresponding to the results obtained using our quantum mechanical calculations fall on top of each other.

Table IV. Average Deviations for Mixture<sup>a</sup>

Associating compound	Diluent	<i>T</i> (°C)	<i>P</i> (mm Hg)	Method	<i>k<sub>H</sub></i>	$\Delta P$	$\Delta y$
Propionic acid	<i>n</i> -Heptane	25	19-45	SAFT	0.017	0.47	0.031
				H-F	0.069	0.45	0.009
				DFT	0.076	0.41	0.018
Propionic acid	<i>n</i> -Heptane	50	17-142	SAFT	0.010	1.00	0.036
				H-F	0.059	1.09	0.009
				DFT	0.065	1.82	0.018
Acetic acid	<i>n</i> -Heptane	30	20-69	SAFT	0.057	2.39	0.079
				H-F	0.090	2.92	0.018
				DFT	0.099	2.89	0.027
Acetic acid	Benzene	25	15-95	SAFT	0.029	0.82	0.018
				H-F	0.060	0.28	0.008
				DFT	0.069	0.30	0.010
Formic acid	Benzene	25	42-119	SAFT	0.109	1.10	0.081
				H-F	0.126	2.55	0.076
				DFT	0.136	3.89	0.069
Methanol	CHCl <sub>3</sub>	35	230-369	SAFT	-0.038	4.67	0.014
				H-F	-0.018	2.71	0.008
				Method	<i>k<sub>H</sub></i>	$\Delta T$	$\Delta y$
Propionic acid	Benzene	80-141	760	SAFT	-0.006	2.54	0.004
				H-F	0.032	0.51	0.005
				DFT	0.039	1.11	0.006
Propionic acid	CCl <sub>4</sub>	77-137	760	SAFT	-0.002	1.81	0.009
				H-F	0.027	0.55	0.009
				DFT	0.028	0.78	0.007
Acetic acid	CCl <sub>4</sub>	76-112	760	SAFT	0.035	1.73	0.014
				H-F	0.068	0.33	0.009
				DFT	0.074	0.39	0.009
Formic acid	1-C <sub>3</sub> H <sub>7</sub> Cl	46-101	760	SAFT	0.109	8.66	0.125
				H-F	0.118	7.20	0.114
				DFT	0.074	6.54	0.110
Methanol	Benzene	57-81	760	SAFT	0.039	0.80	0.015
				H-F	0.028	0.21	0.008
Methanol	<i>n</i> -Pentane	30-65	760	SAFT	0.022	1.57	0.045
				H-F	0.013	1.81	0.048

<sup>a</sup>Data from *Vapor-Liquid Equilibrium Data Collection*, J. Gmehling and U. Onken, eds. (DECHEMA, Frankfurt/Main, Flushing, NY, 1977).

not present these results graphically. The average errors in calculated vapor mole fraction and calculated temperature or pressure for these systems using parameters from the original SAFT and from our methods are presented in Table IV.

### 3.2.2. Mixtures Including Methanol

We initially studied two methanol-containing azeotropic systems: methanol + chloroform (Fig. 5), and methanol + benzene (Fig. 6), and only used parameters derived from the results of our H-F calculations in these fits, as we could not obtain a satisfactory description of pure methanol using the results of the DFT calculations. In both of these cases, as with mixtures involving acids, the parameters derived from our H-F calculations yielded better correlations of the mixture data than did the SAFT model with additional adjustable parameters. Unlike the case for acids, however, here using our parameters results in smaller values of the binary interaction parameters. The negative values of  $k_{ij}$  for the methanol +  $\text{CHCl}_3$  mixture may indicate that a small degree of cross-dimerization is occurring. We have also investigated a third azeotropic system, methanol + *n*-pentane. However, in this case the two parameter sets performed nearly identically, so we do not present the results graphically. The average

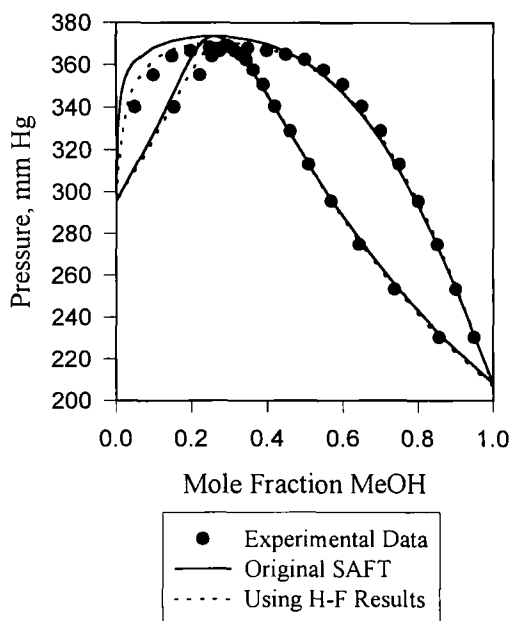


Fig. 5. Bubble pressure calculations for the azeotropic system methanol +  $\text{CHCl}_3$  at  $35^\circ\text{C}$ .

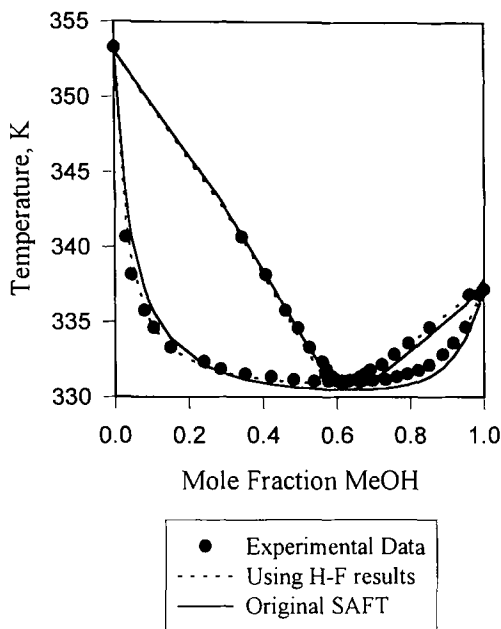


Fig. 6. Bubble temperature calculations for the azeotropic system methanol + benzene at 760 mm Hg.

errors in calculated vapor mole fraction and calculated temperature or pressure for the systems involving methanol are also presented in Table IV.

#### 4. CONCLUSIONS

This work shows the applicability of quantum mechanically derived thermodynamic parameters of association in describing the phase behavior of mixtures containing hydrogen-bonding fluids. In earlier work, we used the results of our quantum-mechanical calculations to fit pure-component vapor pressure and liquid density data for a number of associating compounds using the SAFT model with a reduction in the number of adjustable parameters and little or no loss of accuracy. In this work, we have shown that the use of the pure-component SAFT parameters derived from our quantum-mechanical calculations results in correlations of mixture VLE data without a loss of accuracy, and frequently improved accuracy, compared to the original SAFT parameters.

For mixtures involving acetic or propionic acids, our parameter sets require larger binary interaction parameters than the original SAFT parameters, probably as a result of the high degree of association in these

fluids. For the highly nonideal mixtures involving formic acid, all of the parameter sets require large binary interaction parameters. However, when correlating data for mixtures including methanol, our H-F parameter sets needed smaller binary interaction parameters to achieve comparable (or superior) fits of experimental VLE data.

## ACKNOWLEDGMENTS

The authors would like to thank the National Science Foundation (Grant CTS-9123434) and the Department of Energy (Grant DE-FG02-93ER13436) for financial support of this research. J.W. would like to thank the National Science Foundation for a Pre-Doctoral Fellowship.

## REFERENCES

1. J. P. Wolbach and S. I. Sandler, submitted for publication (1996).
2. J. P. Wolbach and S. I. Sandler, submitted for publication (1996).
3. W. G. Chapman, G. Jackson, and K. E. Gubbins, *Mol. Phys.* **65**:1057 (1988).
4. W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, *Fluid Phase Equil.* **52**:31 (1989).
5. W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, *Ind. Eng. Chem. Res.* **29**:1709 (1990).
6. M. S. Wertheim, *J. Stat. Phys.* **35**:19 (1984).
7. M. S. Wertheim, *J. Stat. Phys.* **35**:35 (1984).
8. M. S. Wertheim, *J. Stat. Phys.* **42**:459 (1986).
9. M. S. Wertheim, *J. Stat. Phys.* **42**:477 (1986).
10. S. H. Huang and M. Radosz, *Ind. Eng. Chem. Res.* **29**:2284 (1990).
11. I. G. Economou and M. D. Donohue, *AIChE J.* **37**:1875 (1991).
12. I. G. Economou and M. D. Donohue, *Ind. Eng. Chem. Res.* **31**:2388 (1992).
13. J. P. Wolbach and S. I. Sandler, submitted for publication (1996).
14. S. S. Chen and A. Kreglewski, *Ber. Bunsenges Phys. Chem.* **81**:1049 (1977).
15. A. Kreglewski, *Equilibrium Properties of Fluids and Fluid Mixtures*, Texas Engineering Experiment Station (TEES) Monograph Series (Texas A&M University Press, College Station, 1984), pp. 117-121.
16. S. H. Huang and M. Radosz, *Ind. Eng. Chem. Res.* **30**:1994 (1991).