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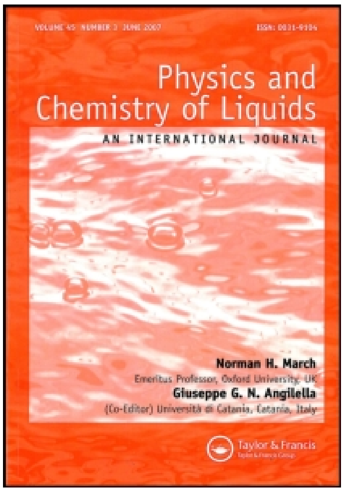

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Excess Thermodynamic Properties of Ternary Fluid Mixtures from Molecular Dynamics Simulation and Van Der Waals One-Fluid Theory

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EXCESS THERMODYNAMIC PROPERTIES OF TERNARY FLUID MIXTURES FROM MOLECULAR DYNAMICS SIMULATION AND VAN DER WAALS ONE-FLUID THEORY

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In this paper, we report isothermal-isobaric molecular dynamics simulation results for total and excess thermodynamic properties of three selected nonideal ternary fluid mixtures, in which particles interact via a Lennard-Jones pair potential. In these mixtures, size parameters of the components are kept to be the same, but energy parameters of the components differ significantly. Simulation results are reported for mixture density, internal energy, excess Gibbs free energy, excess volume and excess enthalpy of equimolar ternary mixtures as a function of temperature and pressure. The excess Gibbs free energy is obtained directly using the coupling parameter charging approach, which avoids the cancellation or magnification of errors in the simulation. These simulation results are used to check the accuracy of a form of the van der Waals one-fluid theory, which uses an accurate equation of state for the pure fluids. Van der Waals one-fluid theory is successful in predicting total and excess properties of these nonideal mixtures within simulation uncertainties.

Keywords: Computer simulation; excess thermodynamic properties; ternary fluid mixtures; van der Waals one-fluid theory

1. INTRODUCTION

Thermodynamic properties of multicomponent mixtures are important to the design and efficient operation of many industrial processes,

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such as enhanced oil recovery, supercritical extraction, biotechnology, coal-rich gas processing and coal-based feedstock chemical processing. Excess thermodynamic properties play key roles in the understanding of how intermolecular forces cause nonidealities in fluid mixtures, and they are also important to determine phase equilibria in fluid mixtures. In fluid mixtures consisting of spherical molecules, nonideal solution behavior is attributed solely to differences in the molecular size and energy parameters appearing in the potential functions. Such mixtures are usually modeled using the Lennard-Jones (LJ) potential function because the LJ fluid gives a reasonable respresentation of simple fluids and is the best studied potential from simulation and theory. This potential is used as the reference system in perturbation theories of molecular fluid mixtures [1–4]. Therefore, accurate computer simulation results for excess properties and phase equilibria of nonideal LJ mixtures are required to test the accuracy of statistical theories. So far, simulation studies have been devoted to evaluate excess properties and phase equilibria of binary mixtures only [5–19]. Only recently, Gibbs ensemble Monte Carlo simulation results for vapor/liquid phase equilibria in ternary mixtures have been reported [20, 21]. Simulation results for the excess thermodynamic properties have not been published in the literature. Excess thermodynamic properties play important role in judging theories because they are very sensitive to the strength of unlike molecular interactions. Therefore, accurate simulation results for the excess thermodynamic properties are also needed to examine the accuracies of statistical theories [22].

The excess property M^E at a given temperature, T, and pressure, P, is defined as

$$M^E = M - \sum_{\alpha} X_{\alpha} M_{\mathrm{pure},\alpha} \tag{1}$$

where M is a generic extensive thermodynamic property of the mixture, and $M_{\mathrm{pure},\alpha}$ is the corresponding property of the pure component α, both at the same (T, P). X_{α} is the mole fraction of component α.

If the excess properties are obtained from eqn. (1), there may be a cancellation of error or a magnification of error because properties of the mixture and the pure components in simulations are determined independent of each other. Moreover, excess Gibbs free energy is difficult to obtain from simulations. Several methods have been proposed in the past to obtain free energy from simulations [23–25]. One of the most reliable routes to the free energy is based on the coupling parameter charging approach [26, 27]. A version of the coupling parameter method was used extensively in Monte Carlo simulation studies of moderately nonideal mixtures [28–31], essentially at zero pressure. However, that version of the method required values for the free energies of the pure components. Later, the coupling parameter method was revised so as to eliminate the need of the pure component free energies [32]. Subsequently, the revised method was tested using molecular dynamics simulations of several binary nonideal mixtures over a range of temperature, pressure and composition [5, 6, 10]. This method has been found to be highly accurate in obtaining excess free energy of even strongly nonideal mixtures and can be applied to mixtures in which particles may differ in any number of potential parameters [9]. Once the free energy is known, excess volume and excess enthalpy can also be evaluated using the coupling parameter method, without the need of pure component properties.

Purpose of the present investigation is to report isothermal-isobaric molecular dynamics simulation results on the total and excess properties of ternary fluid mixtures. In these mixtures, size parameters of components are the same but energy parameters differ significantly. We present simulation results for three excess properties: excess Gibbs free energy (G^E), excess enthalpy (H^E) and excess volume (V^E) along with total density (ρ) and residual internal energy (U^{res}) of mixtures as a function of temperature and pressure. In these simulations, G^E is obtained using the accurate coupling parameter method. These studies would be complementary to experimental and theoretical work because simulations provide the isobaric excess properties. We also examine how accurately the van der Waals one-fluid theory can predict our simulation results.

The paper is organized as follows. The coupling parameter for a ternary mixture is presented in Section 2. Section 3 summarizes the molecular dynamics simulation method. In Section 4, we present van der Waals one-fluid theory based on an accurate equation of state for the pure LJ fluids. In Section 5, we present simulation results and also test the accuracy of the van der Waals one-fluid theory. Finally, conclusion of the paper is presented in Section 6.

2. DETERMINATION OF EXCESS PROPERTIES

Here, we consider a ternary simple fluid mixture of species $\alpha(=A, B, C)$ and $\beta(=A, B, C)$. In this mixture, the total potential energy of interaction (U) is given by the pairwise additive Lennard-Jones (LJ) potentials ($U_{\alpha\beta}$),

$$U = \sum_{\alpha}\sum_{\beta} U_{\alpha\beta} \tag{2}$$

with

$$U_{\alpha\beta} = (2-\delta_{\alpha\beta})\sum_{i<j} 4\varepsilon_{\alpha\beta}\left[(\sigma_{\alpha\beta}/r_{ij})^{12} - (\sigma_{\alpha\beta}/r_{ij})^{6}\right] \tag{3}$$

More specifically, for the ternary mixture U can be written as

$$U = U_{AA} + U_{BB} + U_{CC} + U_{AB} + U_{AC} + U_{BC} \tag{4}$$

In eqn. (3) $\sigma_{\alpha\beta}$ and $\varepsilon_{\alpha\beta}$ are size and energy parameters in the pair potential, respectively, r is the intermolecular separation distance, and $\delta_{\alpha\beta}$ is the Dirac delta function. Unlike size parameters (σ_{AB}, σ_{AC}, σ_{BC}) and energy parameters (ε_{AB}, ε_{AC}, ε_{BC}) are given by the following combination rules (CR),

$$\sigma_{\alpha\beta} = \eta_{\alpha\beta}(\sigma_{\alpha\alpha} + \sigma_{\beta\beta})/2 \tag{5}$$

$$\varepsilon_{\alpha\beta} = \zeta_{\alpha\beta}\sqrt{\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta}\mathrm{n}} \tag{6}$$

where, $\eta_{\alpha\beta}$ and $\zeta_{\alpha\beta}$ are unlike size and energy interaction parameters, respectively. For $\eta_{\alpha\beta} = 1$, eqn. (5) is called Lorentz CR. For $\zeta_{\alpha\beta} = 1$, eqn. (6) is called Berthelot CR. For both $\eta_{\alpha\beta} = 1$ and $\zeta_{\alpha\beta} = 1$, eqns. (5) and (6) are called Lorentz-Berthelot (LB) CR. In these simulations, $\sigma_{AB} = \sigma_{AC} = \sigma_{BC}$, and $\varepsilon_{AA}/k = 120$ K, $\sigma_{AA} = 3.405$ Å.

In general, the excess Gibbs free energy is defined as [5, 6, 32]

$$G^{E} = G_{\mathrm{mixture}}(T, P) - G_{\mathrm{is}}(T, P) \tag{7}$$

where, G_{is} is the free energy of an ideal solution

$$G_{\text{is}} = \sum_{\alpha} X_\alpha G_{\text{pure},\alpha}(T, P) + N k_B T \sum_{\alpha} X_\alpha \ln X_\alpha \tag{8}$$

and $G_{\text{pure},\alpha}$ is the free energy of pure α, and k_B is the Boltzmann's constant.

For a ternary mixture, an alternative expression to eqn. (7) can be given as [5, 32]

$$G^E = X_A(G^{\text{res}}_{\text{mixture}} - G^{\text{res}}_{\text{pureA}}) + X_B(G^{\text{res}}_{\text{mixture}} - G^{\text{res}}_{\text{pureB}}) + X_C(G^{\text{res}}_{\text{mixture}} - G^{\text{res}}_{\text{pureC}}) \tag{9}$$

where G^{res} is the residual free energy of the mixture as the difference between the free energy of the mixture and that of the ideal gas at the same T and P.

Using statistical thermodynamics [33] and the multiple-parameter charging method [9], the excess Gibbs free energy of the n-component mixture (eqn. (9)) in which particles differ in k parameters $\{\lambda_i\}$ is given by

$$G^E = \sum_{\alpha=1}^{n} \sum_{i=1}^{k} X_\alpha \int_{\lambda_\alpha}^{\lambda_m} \langle (\partial U/\partial \lambda_i)_{NPT\lambda_{j\neq i}} \rangle d\lambda_i \tag{10}$$

This expression suggests that all $\{\lambda_i\}$ parameters can be charged separately. However, since G is a state function one can choose to charge all parameters for species α simultaneously. The final value of G^E must be independent of the way in which charging is performed. Hence, eqn. (10) can be written in terms of an arbitrarily chosen parameter λ_i,

$$G^E = \sum_{\alpha=1}^{n} \sum_{i=1}^{k} X_\alpha \int_{\lambda_\alpha}^{\lambda_m} \langle (\partial U/\partial \lambda_i)_{NPT\lambda_{j\neq 1}} \rangle (d\lambda_i/d\lambda_1)\, d\lambda_1 \tag{11}$$

Since during one simulation all $\{\lambda_i\}$ are fixed, all the slopes $(d\lambda_i/d\lambda_1)$ are constant. Therefore, eqn. (11) can be written as

$$G^E = \sum_{\alpha=1}^{n} X_\alpha \int_{\lambda_\alpha}^{\lambda_m} \langle (\partial U/\partial \lambda_i)_{NPT} \rangle d\lambda_1 \tag{12}$$

Thus, one has to evaluate only one integral for each component regardless of the number of parameters. In above equations, angle brackets represent time or ensemble averages at constant (N, P, T). In the 3-component mixture, eqn. (12) can be rewritten explicitly as

$$G^E = X_A \int_1^{\lambda_{m_A}} \langle (\partial U/\partial \lambda_1)_{NPT} \rangle d\lambda_1 + X_B \int_1^{\lambda_{m_B}} \langle (\partial U/\partial \lambda_2)_{NPT} \rangle d\lambda_2 + X_C \int_1^{\lambda_{m_C}} \langle (\partial U/\partial \lambda_3)_{NPT} \rangle d\lambda_3 \tag{13}$$

Each term in eqn. (13) represents a charging process that starts from one of the pure components. In this process, all the potential parameters are charged simultaneously to their values $\lambda_{m\alpha}$ in the mixture of interest. Here, energy ratios corresponding to three components are the only parameters, while size ratios are the same. Each charging process in eqn. (13) involves simultaneously charging two parameters. For example, in order to evaluate the first term in eqn. (13), we start from pure $A(\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon_{CC})$ and charge ε_{BB} and ε_{CC} to their values. The ratio $\lambda_1 = \varepsilon_{BB}/\varepsilon_{AA}$ is chosen to be the independent coupling parameter, and $\varepsilon_{CC}/\varepsilon_{AA}$ is charged simultaneously with λ_1 along the straight line, $\lambda_1 = m_1\,(\varepsilon_{CC}/\varepsilon_{AA}) + b_1$. For this choice of the parameter, the integrand in the first part of the eqn. (13) is given by

$$\langle (\partial U/\partial \lambda_i) \rangle_{NPT\varepsilon_{AA}} = \langle U_{BB} \rangle/\lambda_1 + \langle U_{AB} \rangle/2\lambda_1 + \langle U_{AC} \rangle/2(\lambda_1 - b_1) + \langle U_{BC} \rangle(2\lambda_1 - b_1)/2\lambda_1(\lambda_1 - b_1) + \langle U_{CC} \rangle/(\lambda_1 - b_1) \tag{14}$$

The integrand in the second part of the eqn. (13) is evaluated by setting $\lambda_2 = \varepsilon_{CC}/\varepsilon_{BB}$ and charging along the path $\lambda_2 = m_2\,(\varepsilon_{AA}/\varepsilon_{BB}) + b_2$, and is given by

$$\langle (\partial U/\partial \lambda_2) \rangle_{NPT\varepsilon_{BB}} = \langle U_{CC} \rangle/\lambda_2 + \langle U_{BC} \rangle/2\lambda_2 + \langle U_{BA} \rangle/2(\lambda_2 - b_2) + \langle U_{CA} \rangle(2\lambda_2 - b_2)/2\lambda_2(\lambda_2 - b_2) + \langle U_{AA} \rangle/(\lambda_2 - b_2) \tag{15}$$

Similarly, the integrand in the third part of eqn. (13) is obtained by setting $\lambda_3 = \varepsilon_{AA}/\varepsilon_{CC}$ and charging along the path $\lambda_3 = m_3\,(\varepsilon_{BB}/\varepsilon_{CC}) + b_3$, and is given by

$$\langle(\partial U/\partial\lambda_3)\rangle_{NPT\varepsilon_{CC}} = \langle U_{BB}\rangle/\lambda_3 + \langle U_{AB}\rangle/2\lambda_3 + \langle U_{AC}\rangle/2(\lambda_3 - b_3)$$
$$+ \langle U_{BC}\rangle(2\lambda_3 - b_3)/2\lambda_3(\lambda_3 - b_3) + \langle U_{CC}\rangle/(\lambda_3 - b_3) \quad (16)$$

Along the chosen straight line path, the potential parameters $\{\lambda_i\}$ are related by $(k - 1)$ parameter equation of the form

$$b_k = (\lambda_k^f - \lambda_k^i)/(\lambda_1^f - \lambda_1^i) \quad (17)$$

where, f and i represent the final and initial values of the parameters, respectively. In order to obtain the reliable value of G^E, several simulations are performed, each at a different λ value. The integrands are evaluated from each simulation and the integrals are then computed numerically.

3. MOLECULAR DYNAMICS SIMULATION

We follow the same isothermal-isobaric molecular dynamics simulation method as described for binary mixtures before [5, 6]. Here, we describe briefly the important parameters used in the simulation. Simulations of the integrands, density, pressure and internal energy are performed on ternary mixtures of 300 LJ particles. The pressure in the simulation is controlled using Andersen's method [34]. The temperature is controlled by a momentum scaling method [35]. The NPT equations of motion are solved using a fifth-order predictor corrector algorithm [36]. Each run starts from an FCC lattice structure with initial velocities randomly assigned from a uniform distribution and species labels randomly assigned to particles. The particles are contained in a cubic volume. Periodic boundary conditions and the minimum image criterion are applied [37]. The initial value of volume is determined from van der Waals one-fluid theory, which is described below. In all simulations, component A is composed of the smaller atom. Parameters used in these simulations are given in Table I. The simulation run consists of three phases: (1) equilibrium phase, in which the lattice structure is destroyed and the system relaxed towards equilibrium (2) stabilization phase, in which running average contributions to the pressure are allowed to reach

TABLE I Values of parameters used in the NPT molecular dynamics simulations

Number of atoms	300
Integration time step, $\sigma_{AA}\sqrt{m/\varepsilon_{AA}}$	0.003
Volume inertial parameter, $\sigma^3_{AA}/m^\dagger$	10^{-5}
Potential cut-off radius, $\sigma_{\alpha\beta}$	2.5
Start configuration	FCC lattice
Duration of equilibration phase, time steps	2000–2500
Duration of stabilization phase, time steps	4000
Duration of equilibrium phase, time steps	10000–15000

$^\dagger m$ = mass of an argon atom

nearly constant values and (3) equilibrium phase, in which averages for the integrands, pressure and internal energy are accumulated.

Contribution to the internal energy and pressure beyond the cut-off distance (r_c) are estimated in the usual way,

$$\langle U^c \rangle = \langle U \rangle_{MD} + U_{LR} \tag{18}$$

$$\langle P \rangle = \langle P \rangle_{MD} + P_{LR} \tag{19}$$

with the long range corrections given by

$$U^c_{LR} = 2\pi\rho \sum_\alpha \sum_\beta X_\alpha X_\beta \int_{r_{c\alpha\beta}}^\infty U_{\alpha\beta}(r)\, r^2\, dr \tag{20}$$

$$P_{LR} = -(2/3)\pi\rho^2 \sum_\alpha \sum_\beta X_\alpha X_\beta \int_{r_{c\alpha\beta}}^\infty dU_{\alpha\beta}(r)/dr\, r^3\, dr \tag{21}$$

In eqns. (20) and (21), radial distribution function beyond r_c is taken to be unity. Since the density fluctuates in isobaric simulation, the time averaged value of ρ has been used in these corrections.

Although, analogous procedure can be used to evaluate V^E and H^E in these simulations using coupling parameter method, the values of these properties may not be sufficiently reliable using such a small number of particles (because their terms involve fluctuation terms as well as accumulations of fluctuations). Moreover, excess volumes are very small in these mixtures, so a small uncertainty may cause large relative errors in V^E. Therefore, excess volume and excess enthalpy were obtained from the following equation at the same T and P,

$$V^E = V_{\text{mixture}} - X_A V_{\text{pure A}} - X_B V_{\text{pure B}} - X_C V_{\text{pure C}} \tag{22}$$

$$U^E = U^c_{\text{mixture}} - X_A U^c_{\text{pure A}} - X_B U^c_{\text{pure B}} - X_C U^c_{\text{pure C}} \tag{23}$$

$$H^E = U^E + PV^E \tag{24}$$

where simulations are also performed for the pure fluids at the given temperature and pressure of the mixtures.

4. VAN DER WAALS ONE-FLUID THEORY

Van der Waals one-fluid model was originally suggested by Leland *et al.* [38]. This theory has been applied extensively in the past [39, 40]. In this theory, mixture properties are expressed in terms of the equation of state (EOS) of pure fluids with composition dependent size and energy parameters, given by

$$\sigma_x^3 = \sum_\alpha \sum_\beta X_\alpha X_\beta \sigma_{\alpha\beta}^3 \tag{25}$$

$$\varepsilon_x = \left(\sum_\alpha \sum_\beta X_\alpha X_\beta \varepsilon_{\alpha\beta} \sigma_{\alpha\beta}^3 \right) \Big/ \sigma_x^3 \tag{26}$$

Van der Waals one-fluid theory (VDW1) requires an accurate equation of state for the pure LJ fluids. In the present calculations, we use the recently proposed [41] analytic equation of state for the pure LJ fluids. This equation of state (referred to as KN EOS) is based on a perturbed virial expansion with a theoretically defined temperature dependent hard sphere reference system. It is more accurate and covers much wider range of temperature than the previous equations of state [42, 43]. The important expressions for evaluating thermodynamic properties using KN EOS are given in Appendix I. This version of VDW1 theory has been found very successful in describing excess properties of moderately nonideal binary mixtures [44]. In this paper we test the van der Waals one-fluid theory against our simulation results for ternary mixtures.

5. RESULTS AND DISCUSSION

In this section, we present computer simulation (CS) results for total and excess properties of three ternary mixtures as a function of temperature and pressure. We also examine the accuracy of the van der Waals one-fluid theory by comparing theoretical predictions with our simulation results. Size and energy parameters of the mixtures are contained in Table II.

5.1. Total Properties

Table III contains results for density and residual internal energy of three equimolar ternary mixtures. Mixtures M1 and M2 are considered

TABLE II Potential parameters: size parameter ratios are: $\sigma_{AA}/\sigma_{AA} = \sigma_{BB}/\sigma_{AA} = \sigma_{CC}/\sigma_{AA} = 1$

Mixtures	$\varepsilon_{AA}/\varepsilon_{AA}$	$\varepsilon_{BB}/\varepsilon_{AA}$	$\varepsilon_{CC}/\varepsilon_{AA}$
M1	1	1.200	1.40
M2	1	1.375	1.75
M3	1	1.500	2.00

TABLE III Simulation results for density and internal energy in equimolar ternary mixtures

Mixtures	k_BT/ε_{AA}	$P\sigma^3_{AA}/\varepsilon_{AA}$	$\rho\sigma^3_{AA}$		$U^{res}/N\varepsilon_{AA}$	
			CS	*VDW1*	*CS*	*VDW1*
M1	1.5	1.0	0.699	0.699	−5.64	−5.64
	1.5	1.5	0.738	0.739	−5.93	−5.93
	2.5	1.5	0.520	0.511	−3.78	−3.81
	2.5	4.0	0.703	0.704	−5.09	−5.09
M2	1.5	1.0	0.744	0.743	−6.95	−6.92
	1.5	1.5	0.776	0.773	−7.21	−7.17
	2.5	1.5	0.548	0.549	−4.76	−4.76
	2.5	4.0	0.723	0.722	−6.13	−6.11
M3	1.5	1.0	0.770	0.769	−7.87	−7.83
	1.5	1.5	0.796	0.794	−8.11	−8.07
	2.0	1.5	0.685	0.685	−6.75	−6.72
	2.5	1.5	0.576	0.576	−5.49	−5.49
	2.5	4.0	0.738	0.735	−6.90	−6.85
			AAD	0.28%	–	0.33%

at four different conditions, $(k_BT/\varepsilon_{AA}=1.5,\ P\sigma^3_{AA}/\varepsilon_{AA}=1)$; $(k_BT/\varepsilon_{AA}=1.5,\ P\sigma^3_{AA}/\varepsilon_{AA}=1.5)$; $(k_BT/\varepsilon_{AA}=2.5,\ P\sigma^3_{AA}/\varepsilon_{AA}=1.5)$ and $(k_BT/\varepsilon_{AA}=2.5,\ P\sigma^3_{AA}/\varepsilon_{AA}=4)$. Mixture M3 is considered at five conditions, $(k_BT/\varepsilon_{AA}=1.5, P\sigma^3_{AA}/\varepsilon_{AA}=1)$; $(k_BT/\varepsilon_{AA}=1.5,\ P\sigma^3_{AA}/\varepsilon_{AA}=1.5)$; $(k_BT/\varepsilon_{AA}=2.0,\ P\sigma^3_{AA}/\varepsilon_{AA}=1.5)$; $(k_BT/\varepsilon_{AA}=2.5,\ P\sigma^3_{AA}/\varepsilon_{AA}=1.5)$, and $(k_BT/\varepsilon_{AA}=2.5,\ P\sigma^3_{AA}/\varepsilon_{AA}=4)$. In mixture M3 energy ratios are larger than those in mixtures M1 and M2, thus mixture M3 is more nonideal than other two mixtures. Likewise, mixture M2 exhibits more nonideality than mixture M1. Unlike parameters of the mixtures are obtained from LB CR. Errors in simulation values of both density and internal energy are assigned to be ± 1%. In the table simulation results are compared with densities and internal energies obtained from VDW1 theory. For 13 state points, the absolute average deviation between simulation and VDW1 are 0.28% in density and 0.33% in internal energy. These comparisons show that VDW1 is reliable in describing simulation results for total properties of these mixtures, within simulation errors.

5.2. Excess Properties

For the above three mixtures, Tables IV–VI present simulation results for excess Gibbs free energy, excess volume, and excess enthalpy,

TABLE IV Simulation results for excess Gibbs free energy in equimolar ternary mixtures

Mixtures	k_BT/ε_{AA}	$P\sigma^3_{AA}/\varepsilon_{AA}$	G^E (*J/mol*)	
			CS	*VDW1*
M1	1.5	1.0	56 ± 5	59
	1.5	1.5	52 ± 5	55
	2.5	1.5	39 ± 5	42
	2.5	4.0	40 ± 5	43
M2	1.5	1.0	173 ± 10	186
	1.5	1.5	164 ± 10	175
	2.5	1.5	137 ± 10	151
	2.5	4.0	122 ± 10	142
M3	1.5	1.0	285 ± 15	308
	1.5	1.5	265 ± 15	292
	2.0	1.5	243 ± 15	286
	2.5	1.5	238 ± 15	264
	2.5	4.0	208 ± 15	240

TABLE V Simulation results for excess volume in equimolar ternary mixtures

Mixtures	k_BT/ε_{AA}	$P\sigma^3_{AA}/\varepsilon_{AA}$	$V^E(cc/mol)$	
			CS	*VDW1*
M1	1.5	1.0	-0.43 ± 0.18	-0.28
	1.5	1.5	-0.17 ± 0.17	-0.13
	2.5	1.5	-0.22 ± 0.25	0.01
	2.5	4.0	-0.05 ± 0.18	0.01
M2	1.5	1.0	-0.84 ± 0.17	-0.73
	1.5	1.5	-0.53 ± 0.16	-0.38
	2.5	1.5	-0.37 ± 0.23	-0.27
	2.5	4.0	-0.09 ± 0.17	-0.004
M3	1.5	1.0	-1.13 ± 0.17	-1.04
	1.5	1.5	-0.67 ± 0.16	-0.58
	2.0	1.5	-0.90 ± 0.19	-0.83
	2.5	1.5	-0.84 ± 0.22	-0.68
	2.5	4.0	-0.03 ± 0.17	-0.04

TABLE VI Simulation results for excess enthalpy in equimolar ternary mixtures

Mixtures	k_BT/ε_{AA}	$P\sigma^3_{AA}/\varepsilon_{AA}$	$H^E(J/mol)$	
			CS	*VDW1*
M1	1.5	1.0	32 ± 20	60
	1.5	1.5	43 ± 20	62
	2.5	1.5	87 ± 20	89
	2.5	4.0	44 ± 20	61
M2	1.5	1.0	140 ± 20	174
	1.5	1.5	145 ± 20	183
	2.5	1.5	238 ± 20	269
	2.5	4.0	163 ± 20	194
M3	1.5	1.0	251 ± 30	279
	1.5	1.5	263 ± 30	294
	2.0	1.5	291 ± 30	337
	2.5	1.5	389 ± 30	419
	2.5	4.0	221 ± 30	320

respectively. Table IV shows that G^E decreases as pressure increases, for a given temperature. This behavior is moderate in mixture M1, but becomes more pronounced in mixtures M2 and M3, as the mixtures become more nonideal. Similar behavior is seen when the temperature increases for a given pressure, however, temperature effect is more pronounced quantitatively than the corresponding pressure effect.

TABLE VII Simulation results for density, internal energy and excess Gibbs free energy as a function of energy interaction parameter in equimolar ternary mixtures at $k_BT/\varepsilon_{AA} = 1.5$ and $P\sigma^3_{AA}/\varepsilon_{AA} = 1.5$

ζ_{12}	$\rho\sigma^3_{AA}$	$U^{res}/N\varepsilon_{AA}$	$\Delta G^E/N\varepsilon_{AA}$
0.9	0.755	−6.53	0.464
0.94	0.763	−6.77	0.281
0.97	0.768	−6.99	0.140
1.00	0.775	−7.21	0
1.03	0.778	−7.39	−0.143
1.06	0.785	−7.63	−0.289
1.10	0.791	−7.91	−0.487

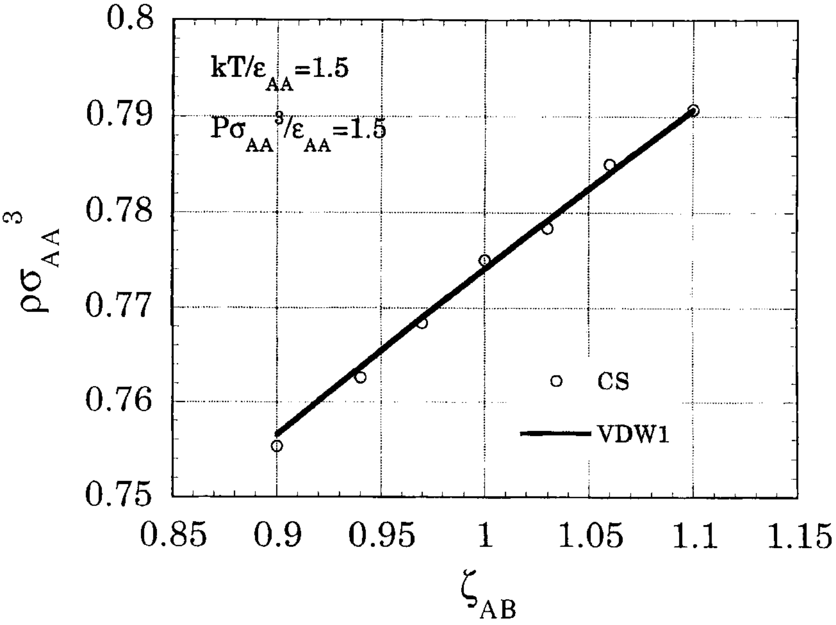

FIGURE 1 Comparison of theoretical and simulation results for density of mixture M2 as a function of unlike energy interaction parameter.

Table V shows that an increase in pressure is responsible for an increase in excess volume in all mixtures for a given temperature. For a given pressure, V^E increases in M1 and M2, while it first decreases and then increases in M3. In Table VI, H^E increases as pressure increases in all the three mixtures when considered at the low temperature, $k_B T/\varepsilon_{AA} = 1.5$. At the higher temperature, $k_B T/\varepsilon_{AA} = 2.5$, H^E is seen to decrease with increasing pressure. On the other hand, H^E is always an increasing function of temperature in all the three mixtures for a given pressure.

Comparison of VDW1 predictions with simulation results in the tables show that VDW1 is the most reliable for mixture M1. As the energy parameter ratio increases, VDW1 starts to slightly deviate from simulation in predicting excess properties, in particular, H^E, of more nonideal mixtures M2 and M3.

In order to study the variation of thermodynamic properties with unlike energy interaction parameters, Table VII contains simulation results for density, internal energy and excess Gibbs free energy (ΔG^E)

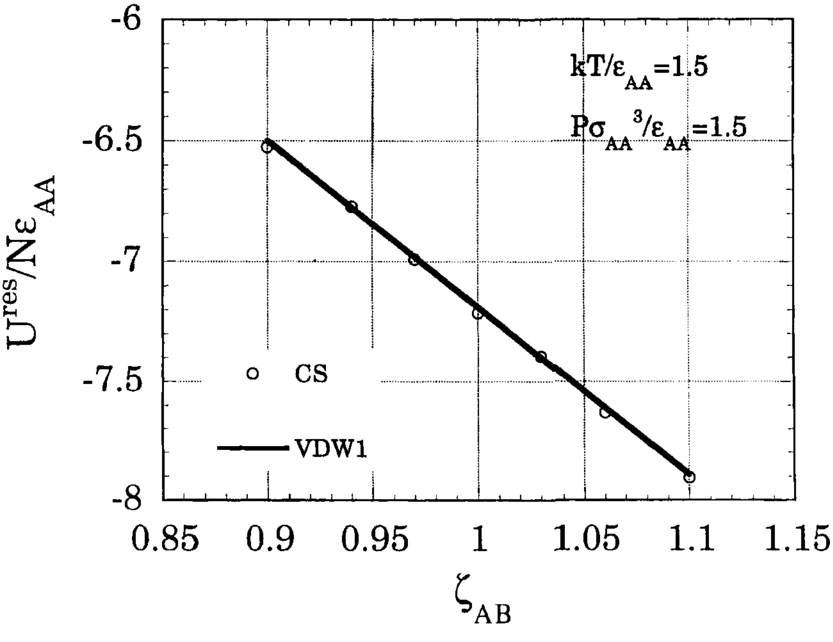

FIGURE 2 Comparison of theoretical and simulation results for residual internal energy of mixture M2 as a function of unlike energy interaction parameter.

of mixture M2 as a function of $\zeta_{12}(\zeta_{12} = \zeta_{13} = \zeta_{23})$. ΔG^E is the difference between excess Gibbs energy of the mixture following LB CR and that of the mixture deviating from LB CR. In these mixtures, unlike energy interaction parameters are equal, but they deviate from Berthelot CR. Size parameters of the components are again the same. As ζ_{12} increases (i.e., as the mixture becomes more nonideal because of the unlike energy effects only), density increases while both internal energy and ΔG^E decrease. This behavior is physically expected. In Figures 1–3, we compare VDW1 and simulation results for density, internal energy and ΔG^E. As the figures show, VDW1 describes these nonideal mixtures very well.

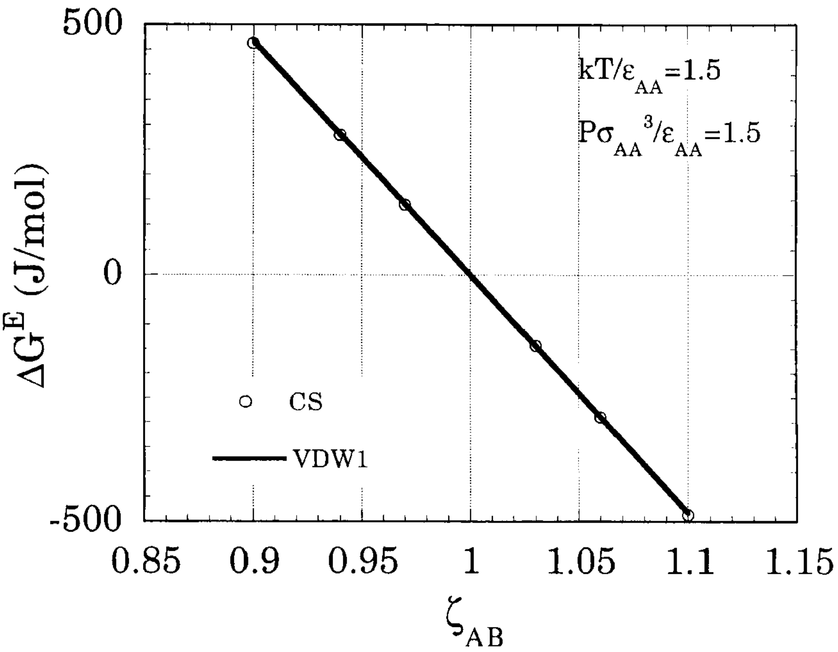

FIGURE 3 Comparison of theoretical and simulation results for the difference between excess Gibbs energy of mixture M2 following LB CR and that deviating from Berthelot CR.

6. CONCLUSIONS

In this paper, we have presented isothermal-isobaric molecular dynamics simulation results for total and excess properties of three equimolar ternary mixtures. These are moderately nonideal mixtures differing only in energy parameter ratios, while size parameter ratios are kept to be the same. Temperature and pressure effects have been investigated. Their effects are significant, in particular, on excess properties of sufficiently nonideal mixtures. The unlike energy interaction parameter is found to significantly affect the total as well as the excess Gibbs free energy. Comparisons of van der Waals one-fluid theory predictions with our simulation results show that VDW1 performs very well in describing total and excess properties of these mixtures. These simulation results are important to test statistical theories of ternary mixtures.

LIST OF SYMBOLS

CS	Computer simulation
EOS	Equation of state
G	Gibbs free energy
H	Enthalpy
KN	Kolafa and Nezbeda EOS
LJ	Lennard-Jones pair potential
P	Pressure
T	Absolute temperature
V	Volume
VDW1	van der Waals one-fluid theory
X	Composition

Greek Letters

ε	Energy parameter in the pair potential
σ	Size parameter in the pair potential

Subscript

A, B, C	Species
α, β	Indices for species

Superscripts

E	Excess property
res	Residual property

APPENDIX I Thermodynamic properties using KN EOS[41]

The residual free energy of the pure LJ fluids is given by

$$A^{\mathrm{res}}/N\varepsilon = A^{\mathrm{HS,res}}/N\varepsilon + \exp(-\gamma\rho^{*2})\rho^* T^* \Delta B_{2,\mathrm{hBH}} + \sum_{ij} C_{ij} T^{*i/2} \rho^{*j} \quad (1.1)$$

with corresponding pressure

$$P\sigma^3/\varepsilon = \rho^* T^* \left\{ Z^{\mathrm{HS}} + \rho^*(1 - 2\gamma\rho^{*2})\exp(-\gamma\rho^{*2})\Delta B_{2,\mathrm{hBH}} + \sum_{ij} jC_{ij} T^{*i/2-1} \rho^{*j} \right\} \quad (1.2)$$

and internal energy

$$U^r/N\varepsilon = \frac{3(Z^{\mathrm{HS}} - 1)}{d_{\mathrm{hBH}}} \frac{\partial d_{\mathrm{hBH}}}{\partial(1/T^*)} + \rho^* \exp(-\gamma\rho^{*2}) \frac{\partial \Delta B_{2,\mathrm{hBH}}}{\partial(1/T^*)} - \sum_{ij}\left(\frac{i}{2} - 1\right) C_{ij} T^{*i/2} \rho^{*j} \quad (1.3)$$

In the above equations, the hard sphere properties are given by

$$Z^{\mathrm{HS}} = (1 + \eta + \eta^2 - 2\eta^3(1+\eta)/3)/(1-\eta)^3 \quad (1.4)$$

and

$$A^{\mathrm{HS,res}}/N\varepsilon = T^*[5\ln(1-\eta)/3 + \eta(34 - 33\eta + 4\eta^2)/(6(1-\eta)^2)] \quad (1.5)$$

with, $\eta = \pi\rho^* d^3_{\mathrm{hBH}}/6$

Functions d_{hBH} and $\Delta B_{2,\mathrm{hBH}}$ are evaluated from the following polynomial

$$f(T^*) = \sum_i C_i T^{*i/2} + C_{\ln} \ln T^* \text{ and } \frac{\partial f(T^*)}{\partial(1/T^*)}$$

$$= -T^* \left(\sum_i \frac{i}{2} C_i T^{*i/2} + C_{\ln} \right) \tag{1.7}$$

Values of the coefficients appearing in the above equations are given below.

Coefficients of d_{hBH} and $\Delta B_{2,\mathrm{hBH}}$:

$d_{\mathrm{hBH}} = f(T^*)$		$B_{2,\mathrm{hBH}} = f(T^*)$	
i	C_i	i	C_i
-2	0.011117524	-7	-0.58544978
-1	-0.076383859	-6	0.43102052
0	1.080142248	-5	0.87361369
1	0.000693129	-4	-4.13749995
ln	-0.063920968	-3	2.90616279
		-2	-7.02181962
		0	0.02459877

Coefficients of the eqns. (1.1–1.3):

i	j	C_{ij}	i	j	C_{ij}	i	j	C_{ij}
0	2	2.01546797	-1	5	93.92740328	-4	2	-13.37031968
0	3	-28.17881636	-1	6	-27.37737354	-4	3	65.38059570
0	4	28.28313847	-2	2	29.34470520	-4	4	-115.09233113
0	5	-10.42402873	-2	3	-112.35356937	-4	5	88.91973082
-1	2	-19.58371655	-2	4	170.64908980	-4	6	-25.62099890
-1	3	75.62340289	-2	5	-123.06669187			
-1	4	-120.70586598	-2	6	34.42288969	γ		1.92907278

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