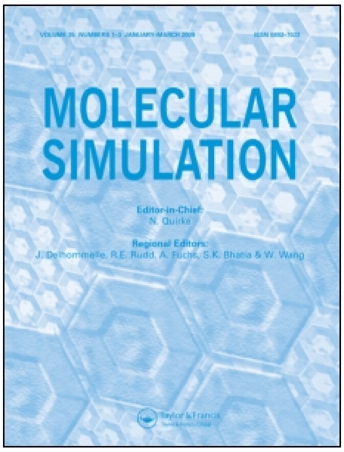

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COMPUTATION CONFIRMS CONTRACTION: A MOLECULAR DYNAMICS STUDY OF LIQUID METHANOL, WATER AND A METHANOL-WATER MIXTURE

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It may be questioned whether potential models that have been developed independently for two different pure compounds would behave properly when used in computer simulations of mixtures of these compounds. Since they are optimized for the pure compounds there is no guarantee whatsoever that the terms describing the interaction between dissimilar molecules are correct. If the simulational and experimental values of several thermodynamical properties of the mixture relative to those of the pure compounds agree closely, however, this strongly indicates that no separate optimizations need be carried out for the mixtures. Here we present the results of isothermal-isobaric Molecular Dynamics simulations of liquid methanol, water and equimolar methanol-water mixtures, using simple point charge models. The potential parameters of the models for the pure liquids had been independently optimized. No adjustment of parameters was made for the mixture, but nonetheless the experimental volume contraction and excess enthalpy upon mixing were reproduced almost perfectly.

KEY WORDS: Molecular dynamics simulations, methanol, water, mixture, excess quantities.

1. INTRODUCTION

Recently we optimized a simple methanol model (OM2) in order to study hydrogen bonding in liquids [1, 2]. We tested the newly developed OM2 model by simulating an equimolar mixture of methanol and SPC water for which the same optimization strategy had been employed as for OM2 methanol [3, 4]. All atoms are described explicitly, except the methyl group which is regarded as a united methyl (Me) atom. Bond distances are fixed. Bending of the methanol Me–O–H angle is allowed; the water H–O–H angle is fixed. Intermolecular interactions are governed by a Lennard-Jones-Coulomb 12-6-1 potential function. Partial charges are centred on the nuclei. The oxygen and methyl atoms have a van der Waals radius determined by C_{12} repulsive and C_6 attractive parameters; for hydrogen these parameters are zero. C_{12}/C_6 parameters for interactions between two dissimilar atoms are defined as the geometrical mean of the C_{12}/C_6 parameters of these two atoms. Other combination rules exist but the results of Haughney *et al.*, who used the arithmetic mean for atomic diameters in their simulations of methanol, show that the differences are negligible in

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Table 1 SPC water and OM2 methanol parameters.

Parameter	*Units*	*Water*	*Methanol*
r(O-H)	Å	1.00	1.033
r(Me-O)	Å	-	1.425
ϕ_0	degrees	109.47	108.53
k_ϕ	kJ/(mol.rad^2)	-	397.5
C_6(OO)	MJ Å^6/mol	2.6169	2.2616
C_6(MeMe)	MJ Å^6/mol	-	8.8758
C_{12}(OO)	GJ Å^{12}/mol	2.6332	2.5231
C_{12}(MeMe)	GJ Å^{12}/mol	-	17.8426
q(O)	e	-0.82	-0.69
q(Me)	e	-	$+0.29$
q(H)	e	$+0.41$	$+0.40$

the case of pure methanol [5]. However, it should be noted that it is not evident *a priori* what the influence on mixtures will be. The complete model is detailed in Table 1.

Because both pure compound models were designed to be used in isobaric simulations and optimized in such a way as to represent the density correctly, a very useful test of transferability is to compare the experimental and simulational density of the mixture. This case is especially interesting because in a real equimolar methanol-water mixture at 298.15 K a volume contraction of 3.44% is observed with respect to the value resulting from interpolation between the molar volumes of pure water and pure methanol [6, 7]. Because the models were also fitted to the experimental heats of vaporization, we felt it would be interesting to investigate whether the experimental excess enthalpy of an equimolar mixture, -0.796 kJ/mol at 298.15 K [7], is represented correctly as well.

2. SIMULATION DATA

Molecular Dynamics (MD) simulations of water, methanol and two independent equimolar methanol-water mixtures were carried out on a Cyber 205 and on a Local Area Vax Cluster, using the GROMOS computer program package [8]. The systems under consideration consisted of 216 molecules in a cubic periodic box and were simulated at constant temperature ($T \approx 298$ K, coupling time constant $\tau_T = 0.1$ ps) and at constant pressure ($P \approx 1$ atm., isotropic pressure scaling, coupling time constant $\tau_P = 0.5$ ps) [1, 9]. The isothermal compressibility values used were 4.6×10^{-10} m^2/N (water), 12.6×10^{-10} (methanol) and 10.1×10^{-10} (mixture). The temperatures were adjusted independently for both compounds in case of the mixtures. A cut-off for the potential of 8.5 Å and a time step of 2 fs were used. The SHAKE procedure [10] was used to conserve intramolecular constraints. In the data collection period data were saved every 50 fs. For the pure liquids, equilibrated starting configurations were obtained from previous fixed-volume simulations. Following equilibration periods of 15 ps (at constant pressure), data were collected during 140 ps. In the case of the mixtures, two independent starting configurations were generated from equilibrated methanol. For 108 randomly chosen molecules the methyl atoms were replaced by hydrogen atoms. In 5 fixed-volume simulations of 0.4 ps each the volume was decreased from the volume of pure methanol to the value for the hypothetical, ideal mixture (where there is no contraction.). The equilibration

Table 2 Experimental and simulational results.[a]

		Temperature	*E(pot)*	*Density*	*Pressure*	*T(meth)*	*T(wat)*
Water	sim.	300.98(0.12)	−41.27(0.03)	0.953(0.001)	1.1(9.6)	-	300.28
	exp.	300.98	−41.68	0.996			
Methanol	sim.	295.92(0.10)	−35.63(0.03)	0.799(0.001)	1.2(4.7)	295.33	-
	exp.	295.92	−34.59	0.789			
Mixture	sim.	297.21(0.08)	−39.27(0.02)	0.879(0.001)	1.3(4.6)	296.01	297.22
	exp.	297.21	−39.00	0.882			

[a]:Sim. and exp. refer to simulation and experiment, and T(meth) and T(wat) to the simulational partial temperatures of methanol and water. Temperatures in K. *E*(pot) in kJ/mol. Density in g/cm^3. Pressure in atm. Standard deviations are given in parentheses.

periods for mixture I were 15 ps (fixed volume) and 52 ps (constant pressure) and the data collection period was 135 ps. For mixture II the equilibration took 28 ps with fixed volume and 15 ps at constant pressure, whereafter data were collected during 110 ps.

The results were in the two cases essentially the same and the weighted averages are presented in Table 2, together with the results from the simulations of the pure liquids. Standard deviations were calculated using the method proposed by Straatsma *et al.* [11]. The pressure fluctuates so rapidly that subsequent values (50 ps apart) are independent and it is therefore not necessary to take correlation into account when calculating its standard deviation. The "experimental" potential energy *E*(pot) equals the experimental heat of vaporization [4, 12] corrected for quantum effects and work upon volume change [see: 2, 4]. The experimental densities were taken from [6, 13 and 14]. The experimental potential energy and density of the mixture were derived from the values for the pure compounds and the excess enthalpy/volume values [6, 7], implicitly assuming that the quantum corrections of the excess enthalpy are negligible. The partial temperatures of water and methanol, *T*(wat) and *T*(meth), have been calculated without taking into account the number of global constraints that in principle should be subtracted from the total number of degrees of freedom [15].

3. DISCUSSION AND CONCLUSIONS

For both water and methanol discrepancies of up to 4% in density and potential energy between the simulational and experimental values are observed. On testing SPC water Postma [4] and Berendsen *et al.* [16] also found differences, but these were smaller. Because the volume varies very slowly and their simulations were rather short (20–25 ps), it is not surprising that they undererstimated the deviations from the fitted value. This implies that the fitting procedure requires long runs, when determining potential parameters for liquids that are to be used in isobaric simulations. The observed differences are also due to different cut-offs for the potential used in the fitting procedure and in the actual simulations. Postma's [4], Berendsen's [16] and our results [2] clearly show that a larger cut-off brings about a larger density and a more negative potential energy. A systematic investigation of the influence of the cut-off would therefore be very useful. The influence of the time step must also be checked, since indications exist that the pressure is affected by the time step used [2]. Until these investigations have been carried out, it seems best only to use parameters in simulations with exactly the same conditions as in the fitting procedure.

Table 3 Excess quantities for an equimolar methanol-water mixture.

	contraction (%)	*excess enthalpy (kJ/mol)*
uncorrected values from the simulations	3.47(0.14)	−0.827(0.026)
values (at 297.21 K) derived from the simulations	3.54	−0.767
experimental values (at 297.21 K)	3.43(0.02)	−0.800(0.008)

Instead of using SPC water, one might consider taking enhanced SPC [16], where the self-energy of the effective induced dipole has been taken into account. This implies using similarly enhanced OM2, which requires full re-optimization. It is very likely, however, that only the absolute value of the energy would change, the excess quantities having the same values.

For the equimolar mixture experiment and simulations are in close agreement, but considering the preceding this is most likely due to a cancellation of errors. On the basis of these results it is therefore impossible to assess whether the interaction between water and methanol is described correctly. The information necessary to make this assessment is present in the data, however. Comparison of simulational and experimental values of thermodynamic quantities of the mixtures relative to the pure liquids provides accurate information about the cross-interaction between the two compounds, given their self-interaction.

In Table 3 two of these relative quantities, volume contraction and excess enthalpy, are detailed. The top row gives values calculated from the data in Table 2. The temperature differences between the different simulations were neglected in this calculation. Values for the density and potential energy of the pure compounds at 297.21 K were calculated using the experimental shifts of these quantities on changing the temperature, assuming that the experimental and simulational shifts are essentially the same. Postma has shown that this assumption is valid for the energy over a range of 100 K [4]. Since the temperature shifts in our case are 4 K at the most, this approximation seems in order. The contraction and excess enthalpy derived from these values are given on the middle row. The bottom row gives the experimental values at 297.21 K [6, 7]. The agreement between the simulational and experimental thermodynamic quantities is very good.

Several authors have reported Monte Carlo simulations for dilute aqueous solutions with methanol mole fractions below 0.8% [17, 18, 19]. They employed different potential models and although they disagreed with respect to the thermodynamics of solvation they all found a cagelike water structure ("iceberg") around the methyl group. There is strong experimental evidence (based, among other data, on diffusion measurements) that the water network progressively disintegrates for mixtures with a methanol content exceeding 30 moles percent [20, 21], so most likely the structures found at high dilution are not preserved in the equimolar mixture. In order to gain insight into the interactions involved here and to determine the cause of the large contraction, it would be interesting to analyse the structure of the mixture on the molecular level. It is also worthwhile to extend the investigation to methanol-water mixtures with several different molar ratios and to mixtures where the contraction is even more pronounced. However, these projects go beyond the scope of this paper and for now it suffices to say that our results show that no parameter optimizations have to be carried out for mixtures, like the one described here, once the parameters for the pure compounds have been determined.

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