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ARTICLE

Density and Surface Tension of Propanol and Propanol-Water Mixtures Using Molecular Dynamic Simulations

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Abstract: Optimized Potentials for Liquid Simulations-All Atoms (OPLS-AA) and Transferable Potentials for Phase Equilibria-United Atom (TraPPE-UA) have been examined with two water models (TIP4P and SPC/E) to estimate the density and the surface tension for unary propanol and binary propanol-water mixtures. While both models predicted the experimental trend of the density for the unary system as a function of temperature and for the binary mixtures as a function of mole fraction of propanol, TraPPE-UA shows better fit with experimental data of pure propanol at low temperatures range (200K-300K). On the other hand, for the surface tension, TraPPE-UA provides a better agreement with the experimental data for pure propanol, while OPLS-AA shows better agreement for the binary mixtures at 300K for the entire mole fraction of propanol (0-1). The density profiles of the mixtures show that the structure of the mixtures changes from core-shell at low mole fractions of propanol to well-mixed at high concentrations of propanol.

Keywords: Molecular dynamics, Surface tension, Liquid density, OPLS-AA, TraPPE-UN.

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Introduction

Molecular dynamic simulation is one of the best methods to study soft matter both quantitatively and qualitatively. Molecular dynamics is a computer simulation method that can be used to study thermodynamic and structural properties of physical systems consisting of a large number of subsystems, by providing a direct path from microscopic information to macroscopic properties. Such systems are aliphatic alcohols and their aqueous solutions, which have attracted the attention of many researchers over the past several years [1-11], due to their large variety of applications in industry, engineering, medical and biological sciences [12, 13]. Studying the density of these systems at different mole fractions is important in determining the nature of these fluids when they are mixed together. From density, one might expect an initial structure of the mixture (well-mixed, core-shell, Russian doll); either miscible or immiscible. On the other hand, studying the surface tension is of great importance for studying many phenomena, such as: nucleation rates, sedimentation, hydrophobic effects, distillation, extraction, absorption, diffusion, among others. Regarding propanol-water mixtures, many scientists have studied this system thoroughly. Vargha-Butler et al. studied the effect of surface tension of the mixture on sedimentation of coal particles [14] and found out that the sedimentation of coal no. 8 *versus* surface tension has two maxima; when the effective surface tension of the coal particles equals the surface tension of the mixture. Raina et al. studied the surface enrichment in alcohol-water mixtures [15] and found out that surface enrichment is considerably more pronounced in

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the case of *n*-butanol and *n*-propanol compared to that of ethanol. Surfaces of alcohol-water mixtures studied by sum-frequency generation vibrational spectroscopy have been reported by Sung et al. [16], who found out that the sum-frequency signal is always larger in the mixture than for pure alcohols. As an example, they found out that the sum-frequency signal of the mixture at a mole fraction of propanol of 0.1 is three times larger than that of pure propanol. Surface tension of alcohol-water mixtures has been measured by Gonzalo et al. [17] from 20-50 C and that of propanol-water mixtures at different temperatures and different mole fractions of propanol was studied by Hoke and Chen [18]. Densities of propanol-water mixtures have been measured thoroughly by Mikhail and Kimel [19].

Computationally, many potential models of alcohol have been developed to produce the right properties. Among those, we found out that the best two models for methanol and ethanol are the OPLS-AA [20] and the TraPPE-UA [21]. In this work, we have calculated the thermodynamic properties of propanol at relatively low temperatures from 200K-300K and water-propanol at room temperature with different mole fractions of propanol mixed with SPC\E [22] and TIP4P-water [23] models. The thermodynamic properties were calculated and compared with experimental published data [17, 18] for density and surface tension, while dynamical and structural properties of the system have been postponed to our forthcoming paper.

Simulation Details

After the good preferences of the TraPPE-UA and OPLS-AA models in reproducing the structural, dynamical and thermodynamic properties of methanol-water and ethanol-water systems [24, 25], we chose these potentials to simulate propanol and propanol-water systems. In both models, propanol is considered to be rigid. Regarding the water potential models, we chose the TIP4P- water and the SPC/E- water models due to their validity of reproducing most of the real water properties. In all our MD simulations, periodic boundary conditions are applied in all directions. The pair intermolecular potential between atoms i and j is the sum of Lennard-Jones (LJ) and Coulomb potential, as follows:

$$V_{ij}(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + 4\epsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right)$$

where ϵ_{ij} and σ_{ij} are the LJ parameters for interaction between atoms of different types. The Lorentz-Berthelot rules are used for the interaction between the unlike atoms: $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$.

In this work, GROMACS package was used to perform all simulations [26]. The molecules are confined first inside a box of dimensions of about 3x3x10 nm^3(see Fig.1), then the box is inserted in the middle of a bigger box of dimensions of 3x3x30 nm^3, to assure vacuum in both sides of the binary mixture with 1000 molecules. For the unary systems, the size of the slap is 3x3x3 nm^3, while the size of the whole simulation box is 3x3x12 nm^3 with a total number of molecules of 600. Our systems are equilibrated for 1ns using Berendsen algorithm [27] under a pressure of 1 bar, followed by 4ns equilibration under a constant volume using Nose-Hoover thermostat [28, 29]. All the data is collected after 10ns and the cutoff radius of interaction is taken as 1.3 nm for OPLS-AA and 1.4 nm for TraPPE-UA [21], for the Leonard Jones potential and for the particle mish Ewald (PME) [30] long-range interaction, respectively.

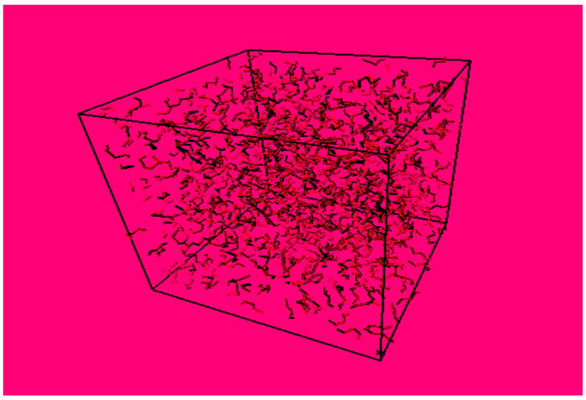

FIG. 1. Simulation box of the water-propanol mixtures (water (blue), propanol (red)).

Results and Discussion

We have computed two different thermodynamic properties of liquid propanol and its binary mixture with water for nine and four site potential models of propanol and two potential models of water.

Density

Vapor- liquid phase diagram is one of the most important quantities that can be used to confirm the validity and accuracy of a new model of soft- matter, through comparing the density with experimental data. Usually, the most published model data starts from room temperature up to an estimated critical temperature. At low temperatures, scaled model is the only rigorous method to estimate the vapor density [31, 32].

We followed the usual method of estimating liquid density by inserting all molecules in a slab within a larger empty box and fitting the profile density to hyperbolic tangent function after assigning zero to the vapor density.

$$\rho(z) = \frac{1}{2}(\rho_l + \rho_v) - \frac{1}{2}(\rho_l - \rho_v)\tanh(\frac{z - z_0}{d})$$

where ρ_l and ρ_v are the bulk densities of the liquid and vapor, respectively, z_0 is the position of the Gibbs dividing surface and d is the width of the interface. The graphic representation of our MD data for both TraPPE-UA and OPLS-AA shows that density decreases linearly with temperature. The results in Fig. 2 indicate that the TraPPE-UA potential model shows a better agreement with the experimental values [17] compared to OPLS-AA. This also occurred in our previous work on methanol and ethanol mixtures with water [24, 25]. This result is not surprising, since TraPPE-UA was modeled originally to give the best vapor- liquid phase diagram.

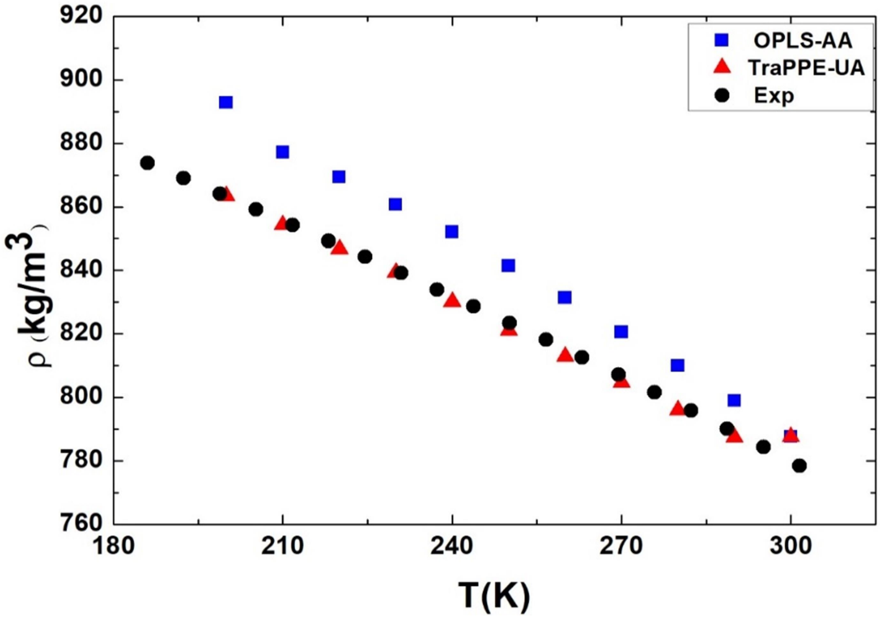

FIG. 2. Density of propanol as a function of temperature: OPLS-AA (blue), TraPPE-UA (red) and experimental data (black).

Fig. 3 shows the density profiles for water, propanol and the mixture at propanol mole fractions of 0.02, 0.08, 0.4 and 0.8. At relatively small values of mole fractions, we have noticed that most of propanol molecules lie near the surface (see the horn shape for the 2% and 8% curves) and very few molecules penetrate inside the water cluster. This behavior indicates that the initial structure of the mixture is a core-shell structure. At higher mole fractions of propanol (see for eg the curves for 40% and 80% curves), propanol molecules tend to lie at the surface and the excess molecules tend to penetrate easily inside the water cluster as indicated by the density curves, which are almost uniform inside the core, indicating that the structure is well-mixed. This eventually is expected to reduce the surface tension of the mixture drastically, as we will elaborate further in Fig. 6. This behavior has been clearly noticed in the supplementary reading of methanol-water mixtures [24].

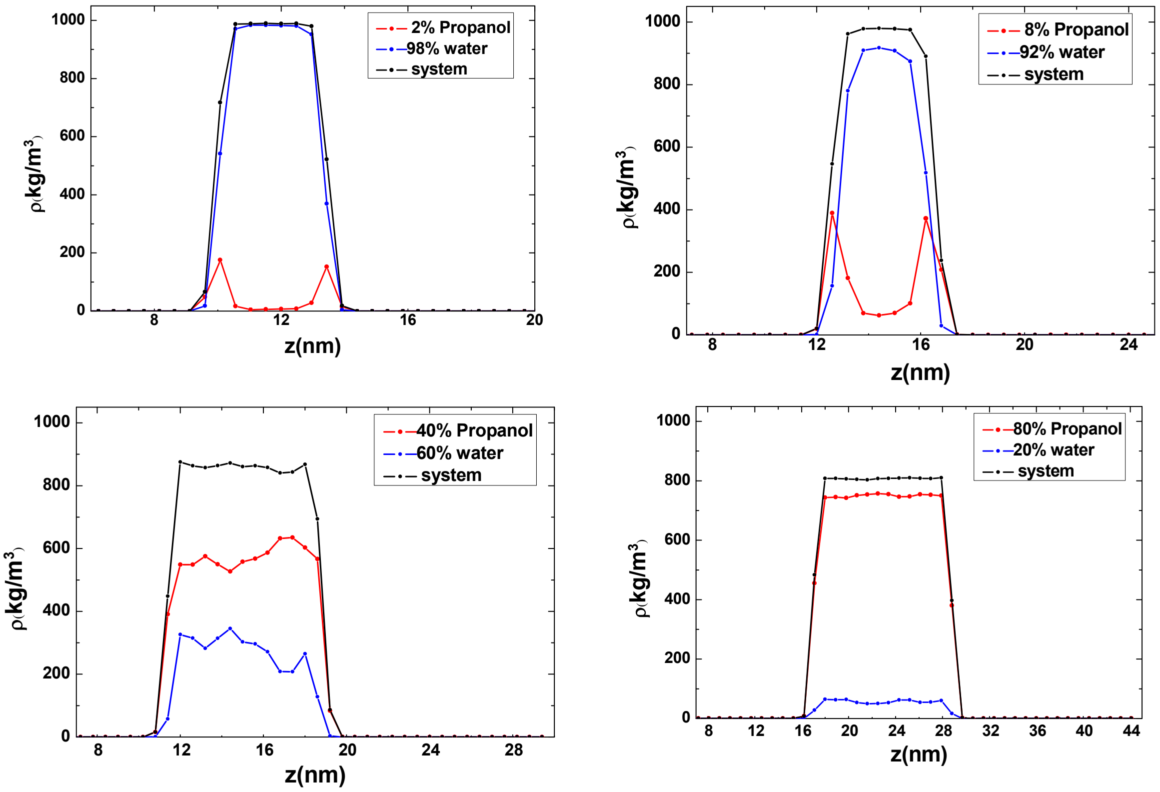

FIG. 3. Density profiles of OPLS-AA with TIP4P-water at mole fractions of propanol of 0.02, 0.08, 0.4 and 0.8.

Fig. 4 shows the density of TIP4P-water, propanol (OPLS-AA and TraPPE-UA) and the system compared to experimental data [19] as a function of mole fraction of propanol. We notice that the total density is linear, which means that the total density follows the relation of mixing rules; i.e., $\rho(x) = (1-x)\rho_{lw} + x\rho_{lp}$, where ρ_{lw} is the density of pure water, ρ_{lp} is the density of pure propanol and x is the mole fraction of propanol. This means that in order to calculate the total density at a specific mole fraction, one needs only the end points and to apply the relation of mixing rules. On the other hand, the small deviation between the total density calculated from the simulation and the total density calculated from the relation of mixing rules might be due to non-additive feature of the intermolecular potential; i.e., the Lorentz rule of mixing might not be totally satisfied [33, 34].

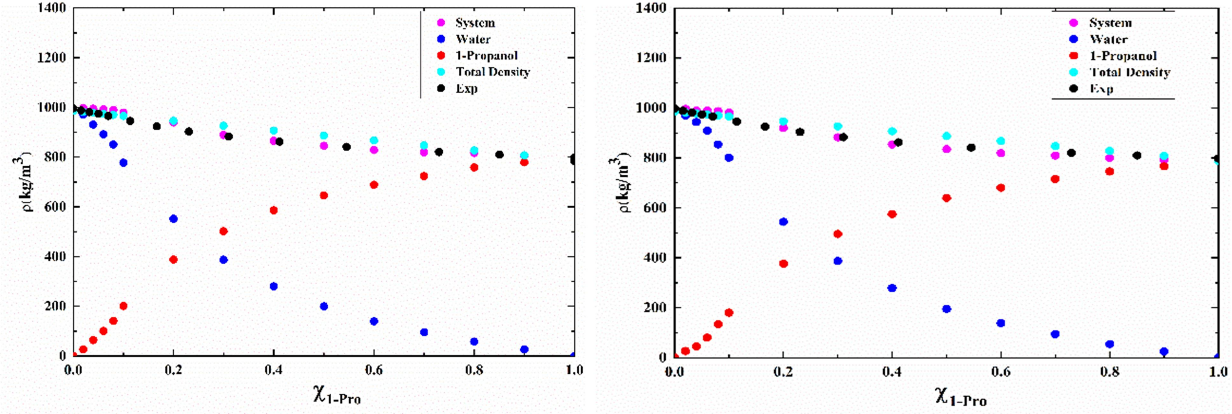

FIG. 4. Density of OPLS-AA propanol (left), TraPPE-UA (right), TIP4P-water (blue), total density from relation of mixing rules (green), system (mangeta) and experimental data (black).

Surface Tension

The net force on the interior molecules of a liquid is zero, since the cohesive forces due to its neighboring molecules cancel each other. On the other hand, the molecules at the surface do not have the same neighboring molecules on all sides; therefore, as a result, the net force on the molecules pulls them inward causing the surface to become under tension.

There are many different methods to estimate the surface tension. In our work, we used the following relation:

$$\gamma = \frac{L_z}{2}\int \left(P_{zz} - \frac{P_{xx}+P_{yy}}{2}\right) dz + 2\pi\sigma^6(\rho_l - \rho_v)^2 \int_0^1 ds \int_{r_c}^{\infty} \coth(\frac{rs}{d}) \frac{3s^3-s}{r^3} dr$$

where $p_{\alpha\alpha}$ is the $\alpha\alpha$ component of the pressure tensor, L_z is the box length in the z direction, ϵ and σ are the Lennard- Jones parameters and r_c is the cutoff radius. The second term has been taken under the consideration of tail correction [35].

To get accurate results of surface tension in the presence of high fluctuations in pressure, we equilibrated our system for a long time, sometimes for 10 ns and then collected the data for further 10 ns.

Fig. 5 shows the effect of temperature on surface tension for pure propanol. It is clear that the surface tension of propanol decreases with temperature in both models, even though the surface tension obtained with TraPPE-UA model has high fluctuations, whereas the OPLS-AA model follows the same trend regarding the linearity behavior. However, the results show that TraPPE-UA model is better in matching the experimental data, whereas the OPLS-AA fail in producing the experimental data over the whole temperature range.

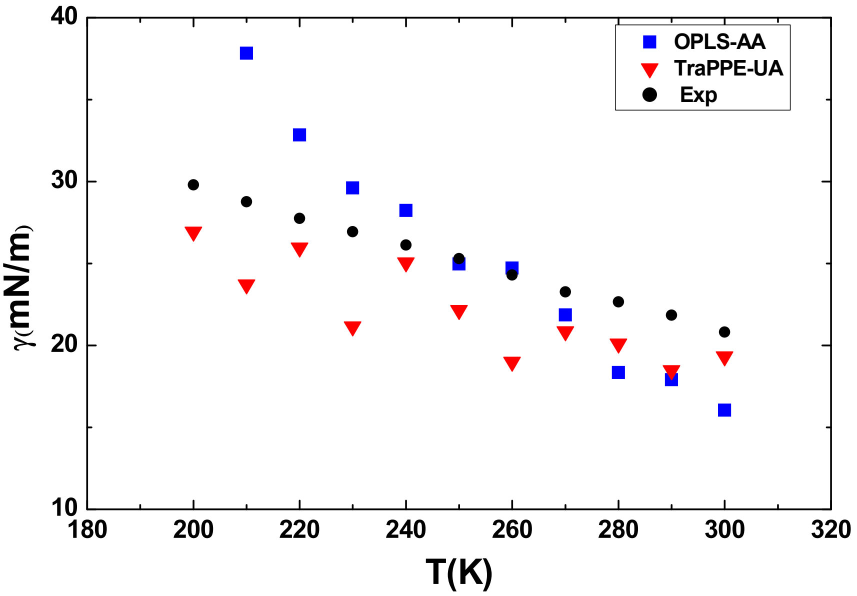

FIG. 5. Surface tension as a function of temperature, OPLS-AA (blue), TraPPE-UA (red) and experimental data (black).

The surface tension of propanol- water mixture was also calculated at different mole fractions of propanol from $\chi_{propanol} = 0.02$ to 0.1 with steps of 0.02 followed by steps of 0.1 up to $\chi_{propanol} = 1$.

Fig. 6 shows our simulation results for the surface tension of the binary system using TraPPE-UA and OPLS-AA force fields, with TIP4P-water compared to the experimental data. At rich water region, both TraPPE-UA and OPLS-AA potential models fit the experimental data very well. At rich propanol region, the OPLS-AA potential model shows better agreement with the experimental data.

We can explain the fast drop of surface tension in Fig. 3 by that for small fractions of propanol, the surface of drop is mostly covered by water molecules and by increasing the mole fraction of propanol, the propanol molecules prefer to spread over the surface, which is a dominating factor in surface tension.

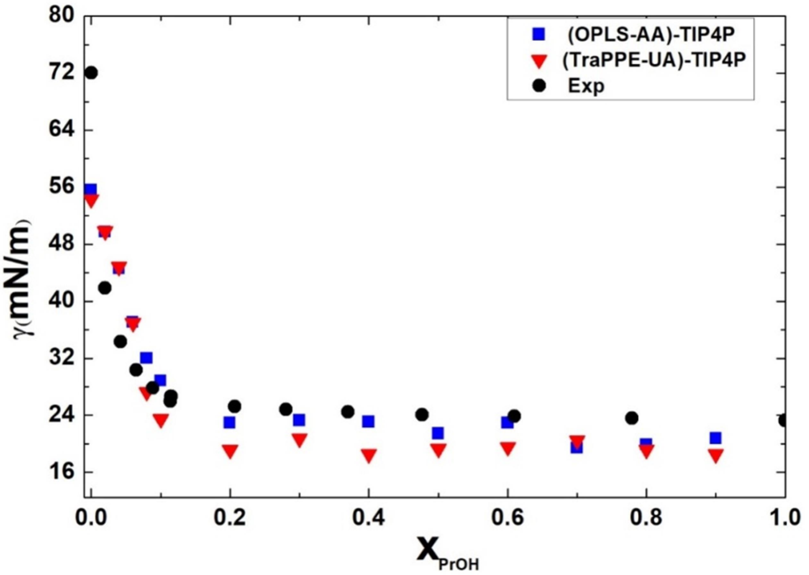

FIG. 6. Surface tension of propanol mixed with TIP4P-water at different mole fractions of propanol compared to experimental data (black), OPLS-AA with TIP4P (blue) and TraPPE-UA with TIP4P (red).

Conclusion

In this work, a series of molecular dynamic simulations (MD) have been performed in order to examine the validity and performance of the (TraPPE-UA) and (OPLS-AA) potential models in producing the thermodynamical properties of pure propanol and its aqueous mixtures by comparing the simulation results for the density and surface tension with the experimental data. Both models are in agreement with the experimental data for the temperature dependence of the density for pure propanol and the mole fraction dependence of the density for the propanol aqueous mixtures. The density profiles of the propanol-water mixtures indicate that at low molar concentrations of propanol (below ~ 30%), the structure of the drop is a core shell, while for high molar concentrations of propanol (above ~ 40%), the structure tends to be well-mixed solution. Moreover, the results of the simulation showed that the total density of the mixture follows the relation of mixing rules.

Regarding the surface tension, (TraPPE-UA) performs better in producing the data for pure propanol, while (OPLS-AA) gives better results for the propanol-water mixtures. The results showed a fast drop in the surface tension as the propanol mole fraction increased, indicating that the propanol molecules prefer to lie on the surface of the water drop.

Overall, this means that one cannot judge the preference of one model over the other without considering the property to be studied. As an example, if one wants to study the nucleation of unary propanol and since nucleation rates depend on the surface tension to the power three, one is advised to use TraPPE-UA. Inversely, when calculating the nucleation rates of the binary water-propanol mixtures, it is more appropriate to use the OPLS-AA model.

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