

Effect of the alkyl chain length on the non-ideality and the microstructure of alcohol binary mixtures

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The total configurational energy U is defined by

$$U = U_{\text{INTRA}} + U_{\text{INTER}} \quad (1)$$

where U_{INTRA} , U_{INTER} are the intramolecular and intermolecular energy contributions, respectively. U_{INTRA} is expressed as

$$U_{\text{INTRA}} = U_{\text{BONDS}} + U_{\text{ANGLES}} + U_{\text{DIHEDRALS}} + U_{\text{NON-BONDED}} \quad (2)$$

such that

$$U_{\text{BONDS}} = k_r(r - r_0)^2, \quad U_{\text{ANGLES}} = k_\Theta(\Theta - \Theta_0)^2 \quad (3)$$

where r is the distance between two atoms, Θ is the valence angle between three atoms, k_r and k_Θ are the strengths of the bonds and valence angle, r_0 and Θ_0 are the equilibrium distance and angle. The dihedral potential is expressed from a triple cosinus potential

$$U_{\text{DIHEDRALS}} = A_0 + 0.5A_1(1 + \cos(\Phi)) + 0.5A_1(1 - \cos(2\Phi)) + 0.5A_3(1 + \cos(3\Phi)) \quad (4)$$

where A_1 , A_2 and A_3 are the strengths of the dihedral angle. All parameters were described from the OPLS force field and can be found elsewhere.¹ The non-bonded terms are evaluated from the electrostatic and Lennard-Jones potential described below.

The intermolecular interactions are composed of repulsion-dispersion and electrostatic contributions that are represented by Lennard-Jones (LJ) and Coulombic (ELEC) potentials, respectively:

$$U_{\text{INTER}} = U_{\text{LJ}} + U_{\text{ELEC}} \quad (5)$$

$$\begin{aligned}
U_{\text{LJ}} &= \sum_{i=1}^{N-1} \sum_{j>i}^N \sum_{a=1}^{N_i} \sum_{b=1}^{N_j} u_{\text{LJ}}(r_{iajb}) \\
&= \sum_{i=1}^{N-1} \sum_{j>i}^N \sum_{a=1}^{N_i} \sum_{b=1}^{N_j} 4\epsilon_{ab} \left[\left(\frac{\sigma_{ab}}{r_{iajb}} \right)^{12} - \left(\frac{\sigma_{ab}}{r_{iajb}} \right)^6 \right]
\end{aligned} \tag{6}$$

where r_{iajb} is the distance between force center a in molecule i and force center b in molecule j , ϵ_{ab} is the energy parameter of the interaction and σ_{ab} is the Lennard-Jones core diameter. N_i is the number of force centers in the molecule i . The LJ parameters for the interactions between unlike sites were calculated using the Lorentz-Berthelot combining rules

$$\epsilon_{ab} = (\epsilon_{aa}\epsilon_{bb})^{1/2} \quad \sigma_{ab} = \frac{1}{2}(\sigma_{aa} + \sigma_{bb}) \tag{7}$$

The electrostatic interactions were calculated using the Ewald sum method from

$$\begin{aligned}
U_{\text{ELEC}} &= \frac{1}{2\epsilon_o V} \sum_{k \neq 0} Q(h) S(\mathbf{h}) S(-\mathbf{h}) \\
&+ \frac{1}{8\pi\epsilon_o} \sum_i \sum_a \sum_{j \neq i} q_{ia} \sum_b q_{jb} \operatorname{erfc}(\alpha r_{iajb}) / r_{iajb} \\
&- \frac{\alpha}{4\pi^{3/2}\epsilon_o} \sum_i \sum_a q_{ia}^2 \\
&- \frac{1}{8\pi\epsilon_o} \sum_i \sum_a \sum_{b \neq a} \frac{q_{ia} q_{ib}}{r_{iaib}} \operatorname{erf}(\alpha r_{iaib})
\end{aligned} \tag{8}$$

where $\operatorname{erfc}(x)$ is the complementary error function and $\operatorname{erf}(x)$ is the error function. α is chosen so that interaction pairs only in the central cell need to be considered in evaluating the second term in Eq. 8. The functions $S(\mathbf{h})$ and $Q(h)$ are defined using Eqs 9 and 10, respectively

$$S(\mathbf{h}) = \sum_i \sum_a q_{ia} \exp(i\mathbf{h} \cdot \mathbf{r}_{ia}) \tag{9}$$

$$Q(h) = \frac{1}{h^2} \exp\left(-\frac{h^2}{4\alpha^2}\right) \quad (10)$$

where the reciprocal lattice vector \mathbf{h} is defined as $\mathbf{h} = 2\pi(l/L_x\mathbf{u}, m/L_y\mathbf{v}, n/L_z\mathbf{w})$ where $\mathbf{u}, \mathbf{v}, \mathbf{w}$ are the reciprocal space basis vectors and l, m, n take values of $0, \pm 1, \pm 2, \dots \pm \infty$. The reciprocal space sum is truncated at an ellipsoidal boundary at the vector $|\mathbf{h}^{max}|$. The convergence factor α is calculated from $\frac{2\pi}{L_x}$. The maximum reciprocal lattice vectors parallel to the surface $|\mathbf{h}_x^{max}|$ and $|\mathbf{h}_y^{max}|$ were fixed to 8 and $|\mathbf{h}_z^{max}|$ to 48. The increase in $|\mathbf{h}_z^{max}|$ is required to accurately account for the long range electrostatic interactions in the direction normal to the interface due to a larger dimension box in this direction.

Partial Structure Factor Calculation

The structure factor ($S^{\text{Liq}}(Q)$) was computed from Eq. 11 where (\mathbf{Q}) is the momentum transfer vector, N_L the number of molecules of liquid, n_L the number of atoms belonging of one liquid molecule, \mathbf{r}_{km} is the vector position $\mathbf{r}_{km} = \mathbf{r}_m - \mathbf{r}_k$ and b_i the coherent diffusion length of atom i . The brackets stand for time and isotropic average carried out over the angles of \mathbf{Q} in spherical coordinates of a sum of the scattering intensity arising from every couples of atoms (θ, ϕ). Thus, the structure factor is expressed by steradians corresponding to the the cross section measured by neutron scattering. $S^{\text{Liq}}(Q)$ is normalized by the number of molecules (N_L) to compare the bulk and confined phases. Then the unit of Eq. 11 is molecules by steradian (molec. sr⁻¹). For more of clarity we will omit the average on θ, ϕ .

$$S^{\text{Liq}}(Q) = \frac{\left\langle \sum_{j=1}^{N_L} \sum_{k=1}^{n_L} \sum_{l=1}^{N_L} \sum_{m=1}^{n_L} b_k b_m \exp(-i\mathbf{Q}\mathbf{r}_{km}) \right\rangle_{\theta, \phi}}{N_L \left(\sum_{i=1}^{n_L} b_i \right)^2} \quad (11)$$

From this relation the partial structure factors of hydrogen atoms of the hydroxyl groups of TBA can be defined as

$$S_X^{\text{Liq}}(Q) = \frac{\left\langle \sum_{j=1}^{N_L} \sum_{m=1}^{n_X} \sum_{l=1}^{N_L} \sum_{k=1}^{n_X} \exp(-i\mathbf{Q}\mathbf{r}_m) \exp(i\mathbf{Q}\mathbf{r}_k) \right\rangle}{N_L n_X} \quad (12)$$

where X is the label of the considered atom (hydrogen, HO) and n_X is the number of X atoms.

Cluster Size Calculation and Hydrogen bond

Prior to define the cluster size calculation, it is necessary to define what is meant by clusters. In this work a cluster is defined as a closed chain of molecules such that the first and last molecules of this sequence are similar contrary to an opened chain where they are different. Calculation of cluster size based on the hydrogen bonds is performed by considering the modified algorithm of Stoddard.² Hydrogen bonds (HB) were computed from the geometrical criteria based on the quantum considerations³ where two molecules are chosen as being hydrogen bonded only if their inter-oxygen distance is less than 3.5 Å, and simultaneously the oxygen-hydrogen is less than 2.5 Å. Both conditions involve that the angle O–H–O is lower than of 30° which is recommended by Luzar and Chandler. However, we have also computed the hydrogen bonds from two previous distance criteria and the angular condition (O–H–O is lower than of 30°). The average number of hydrogen bonds (nHB) calculated from two distances criteria is 1.89548 while calculation from three criteria (distances and angle) provides nHB=1.89453. That allowed us to conclude that only two distances criteria are sufficient to compute hydrogen bonds.

Composition of initial configurations

Table 1: Average length of the cubic simulation box (L) as a function of the number of molecules CHX or TOL (n), alcohol (m) and corresponding molar fraction x . Average uncertainty is calculated around 0.1 Å.

| n | m | x | $L^{EtOH/CHX}$ | $L^{PtOH/CHX}$ | $L^{EtOH/TOL}$ | $L^{PtOH/TOL}$ |
|-----|-----|-----|----------------|----------------|----------------|----------------|
| 500 | 0 | 0.0 | 45.08 | 45.08 | 45.08 | 45.08 |
| 450 | 50 | 0.1 | 44.38 | 45.08 | 44.04 | 44.76 |
| 400 | 100 | 0.2 | 43.66 | 45.08 | 43.32 | 44.78 |
| 350 | 150 | 0.3 | 42.90 | 45.09 | 42.56 | 44.80 |
| 300 | 200 | 0.4 | 42.10 | 45.08 | 41.78 | 44.81 |
| 250 | 250 | 0.5 | 41.29 | 45.07 | 40.97 | 44.82 |
| 200 | 300 | 0.6 | 40.42 | 45.04 | 40.11 | 44.84 |
| 150 | 350 | 0.7 | 39.50 | 45.01 | 39.22 | 44.85 |
| 100 | 400 | 0.8 | 38.52 | 44.99 | 38.30 | 44.87 |
| 50 | 450 | 0.9 | 37.46 | 44.95 | 37.34 | 44.88 |
| 0 | 500 | 1.0 | 36.28 | 44.89 | 36.28 | 44.89 |

References

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- (2) Stoddard, S. Identifying Clusters in Computer Experiments on Systems of particles. *J. Comput. Phys.* **1978**, *27*, 291.
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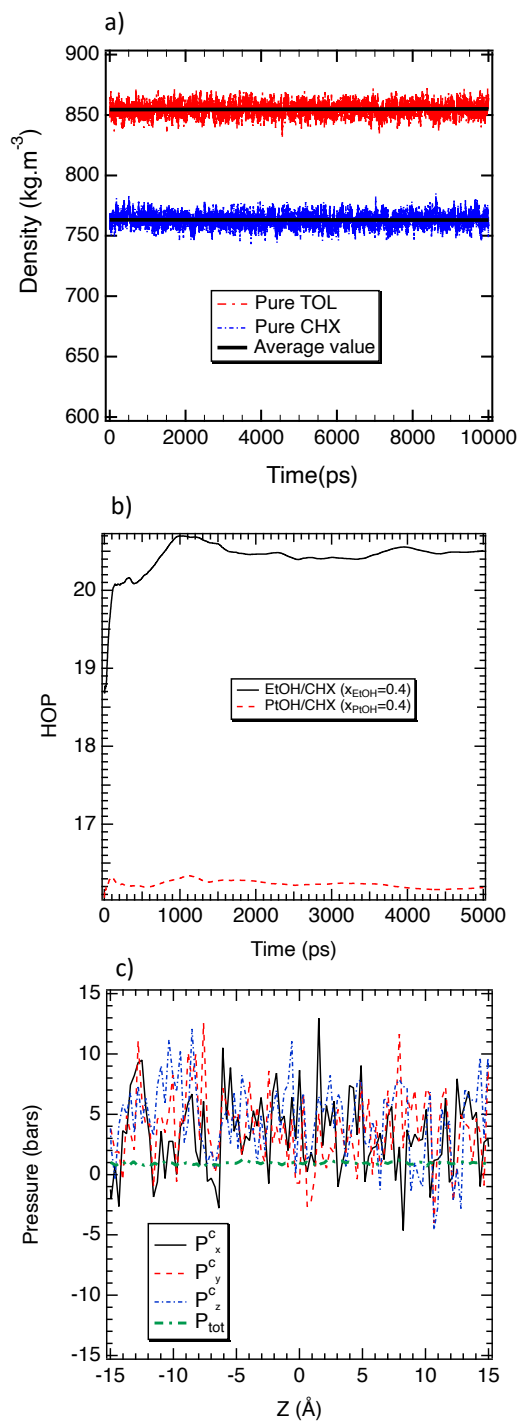


Figure S1: Density, excess density and HOP of PrOH (a, b, c) and BuOH (d, e, f) mixtures.

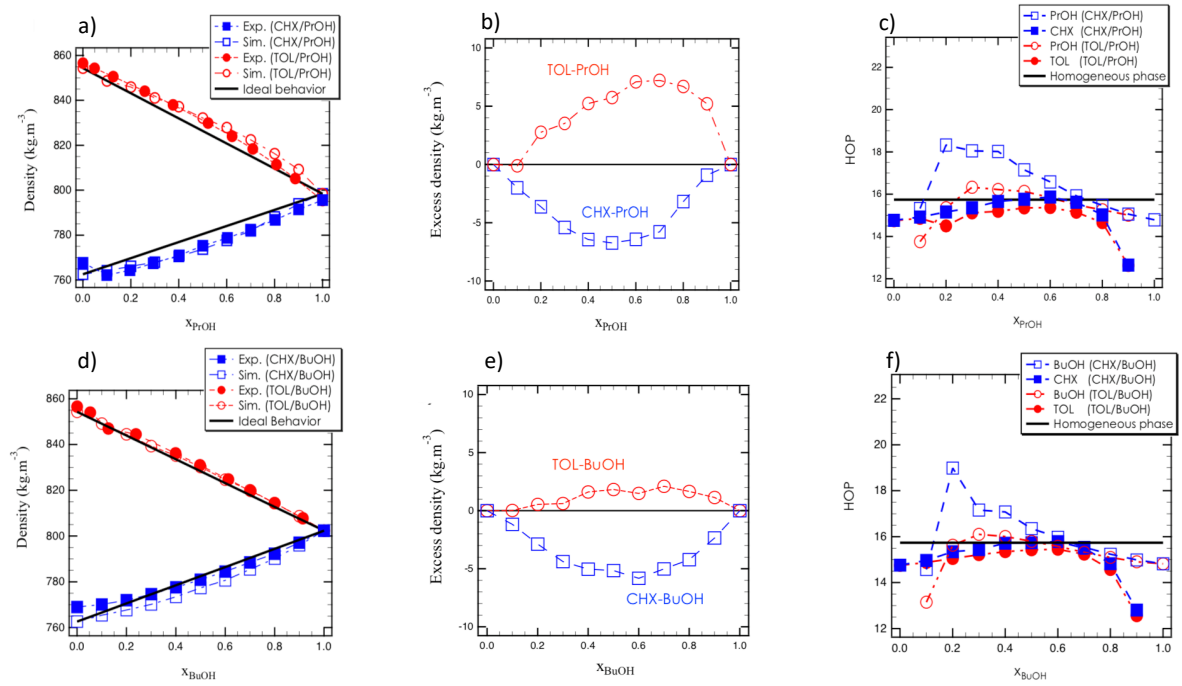


Figure S2: Density, excess density and HOP of PrOH (a, b, c) and BuOH (d, e, f) mixtures.

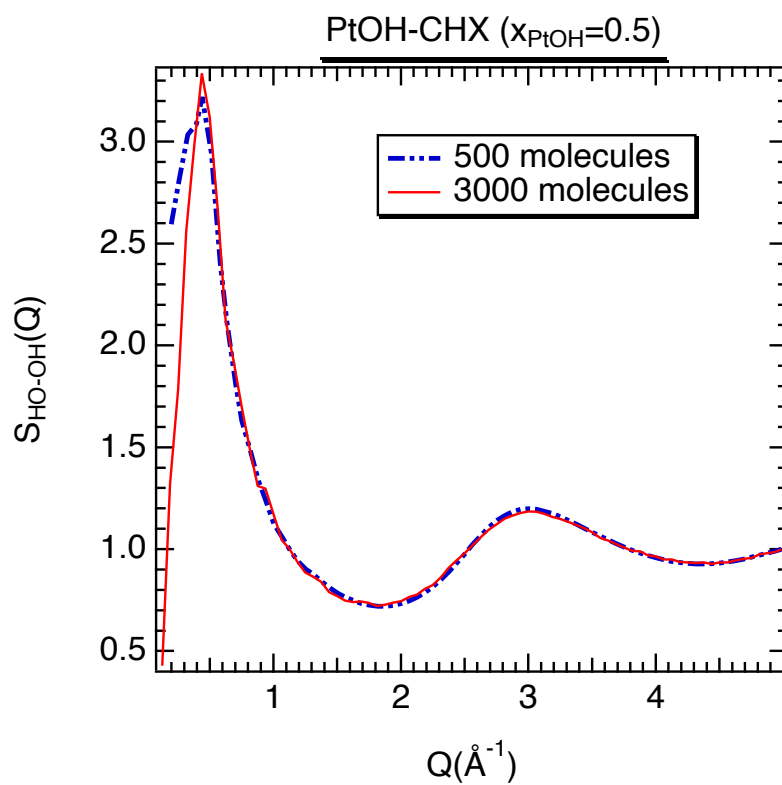


Figure S3: Partial structure factor ($S_{\text{HO-OH}}(Q)$) of PtOH/CHX for a molar fraction $x_{\text{PtOH}}=0.5$ for two configurations of total molecules number of 500 and 3000.