Supplementary Information

Ionic Hydration-Induced Evolution of Decane-Water Interfacial Tension

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1. Model and methods

1.1 Interaction potentials

1.1.1 OPLS All-Atom force field

In this paper, the OPLS All-Atom (OPLS-AA) force field\(^1\) which can accurately describe the thermodynamic properties of organic liquids is employed to express the interactions between decane molecules. This force field is made up of four parts, *i.e.* non-bonded interactions, bond stretching, angle bending and torsion interactions:

\[
E = E_{ab} + E_{\text{bond}} + E_{\text{angle}} + E(\phi).
\]  
(S1)

The non-bonded interaction between \(a\) and \(b\) atom includes the standard 12/6 Lennard-Jones and Coulombic pairwise interactions, given by

\[
E_{ab} = 4\epsilon \left[ \left( \frac{\sigma}{r_{ab}} \right)^{12} - \left( \frac{\sigma}{r_{ab}} \right)^{6} \right] + \frac{C q_a q_b}{\chi r_{ab}^{12}} \quad (r_{ab} < r_{\text{cut}}),
\]  
(S2)

where \(\epsilon\) is the depth of potential well, \(\sigma\) the distance at which the inter-atomic potential is zero, \(r_{\text{cut}}\) the cut-off radius, \(C\) an energy-conversion constant, \(q_a\) and \(q_b\) the charges of atom \(a\) and \(b\), and \(\chi\) is the dielectric constant. While \(r_{ab}\) is greater than \(r_{\text{cut}}\), we use the Particle-Particle Particle-Mesh (PPPM) method to calculate the long-range electrostatic interactions. Potential parameters between the crossing atoms are obtained based on the Lorentz-Berthelot mixing rule,

\[
\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}, \quad \epsilon_{ij} = \sqrt{\epsilon_{ii} \epsilon_{jj}},
\]  
(S3)

All the LJ potential parameters are listed in Table S1.

Table S1. LJ potential parameters used in the simulations.

<table>
<thead>
<tr>
<th></th>
<th>(\epsilon) (eV)</th>
<th>(\sigma) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-O</td>
<td>(6.611 \times 10^{-3})</td>
<td>3.1507</td>
</tr>
<tr>
<td>H(H(_2O))-H(H(_2O))</td>
<td>(1.999 \times 10^{-3})</td>
<td>0.4000</td>
</tr>
</tbody>
</table>
The bond stretching and angle bending in the molecules are described by the harmonic potential as follows,

\[ E_{bond} = K_{bond} (r_{ab} - r_0)^2 , \tag{S4} \]

\[ E_{angle} = K_{angle} (\theta - \theta_0)^2 , \tag{S5} \]

where \( K_{bond} \) and \( K_{angle} \) are the bond and angle coefficients which are related to energy, \( r_0 \) is the equilibrium bond distance, and \( \theta_0 \) is the equilibrium value of bond-angle.
The last term of the OPLS-AA potential is the torsion interaction, which are described by the *opls* dihedral style in our simulations. The form of *opls* dihedral style is as follows,

\[
E(\phi) = \frac{V_1}{2} [1 + \cos(\phi)] + \frac{V_2}{2} [1 - \cos(2\phi)] + \frac{V_3}{2} [1 + \cos(3\phi)],
\]  

(S6)

where \(V_1\), \(V_2\) and \(V_3\) are the coefficients defined for dihedral. The detailed parameters of OPLS-AA potential can be found in Reference S2.

1.1.2 TIP3P water model

In this study, we employ the TIP3P model to simulate the interactions between water molecules. The TIP3P water model is proven to be efficient and can precisely predict the structure and dynamics of the water phase. It assigns the charge and LJ parameter for each atom of the water molecule. Additionally, the *harmonic* bond and angle style are utilized to describe the O-H bond and the H-O-H angle. More detailed description and parameters can be found in Reference S3.

1.2 Simulation details

In this paper, we adopt the Nose-Hoover method to keep the system balanced at specific temperature and pressure in the isothermal-isobaric (NPT) ensemble. The \(T_{\text{damp}}\) parameter determining the speed of the relaxation of temperature is a value of 0.2, while the \(P_{\text{damp}}\) determining the time scale on which pressure is relaxed is a value of 1. It is noteworthy that the good choice for the value of \(P_{\text{damp}}\) is about 1000 timesteps. In the case of lower value of \(P_{\text{damp}}\), pressure and volume would fluctuate severely; in the case of higher value of \(P_{\text{damp}}\), the equilibrium for pressure would be time-consuming. In order to reduce the storage requirements for data processing, the coordinates of ions and molecules are output every 25000 timesteps, i.e. 2.5 ps.

Because of the charge properties of ions, the long-range Coulombic interactions between ions or molecules play an important role in the simulation systems. Thus, in our simulations, we adopt the PPPM solver to calculate the long-range Coulombic force. In this method 3d FFTs is used to solve Poisson’s equation on the mesh where atom charge is mapped, and then electric fields are interpolated on the mesh points back to the atoms. The PPPM solver is a more excellent method to reduce the computation time and memory storage, because it scales as Nlog(N) where N is the total atom numbers, which is far less than the
Ewald summation \(N^{\frac{3}{2}}\). The accuracy of PPPM method is 0.01 and the grid size of the mesh is \(10 \times 10 \times 28\) in the simulations.

### 1.3 Definition of interfacial thickness

As stated in the manuscript, we use the following hyperbolic tangent function to fit the density distribution curve of water and decane molecules.

\[
\rho_i(z) = \frac{\rho_{i,\text{bulk}}}{2} - \frac{\rho_{i,\text{bulk}}}{2} \tanh \left( \frac{2(z - z_0)}{d} \right),
\]

where \(\rho_i\) is the density, \(z_0\) is the position of Gibbs interface, and \(d\) is the alterable parameter concerning the interfacial thickness.

When we obtain the fitting curves, we employ the “90-10” interfacial thickness criterion. The interfacial thickness is defined as the distance between the positions where the densities of water or decane respectively reach 90% of their bulk densities. It is an ordinary practice to determine the interfacial thickness of the liquid-vapor or liquid-liquid interface.

### 1.4 Model validation

In our validation, firstly, by means of the fitting curves of the density profile we get the bulk densities of the water and decane phase, and compare them with the actual density under different temperature and pressure conditions. Table S2 shows the comparison results. Our results are very close to the actual densities of the water and decane liquid under different conditions.

Further, we compare our simulated IFT of the decane-water interface with the results by other researchers\(^4\text{-}11\), including the simulated and experimental value, as shown in Fig. S1. Note that the simulated and experimental conditions of temperature, pressure and ion concentration in the referenced studies are a bit different from our simulation conditions. Moreover, the comparison of our results with the experimental results under high temperature or pressure is done, as shown in Table S3. As you can see, our simulated results of IFT are slightly smaller than the experimental results. We attribute this phenomenon to the difference in the temperature or pressure of the experiments. It is worth noting that the decane-water interfacial tension is sensitive to the inevitable impurities in the experiments, which we think play a key
role for the higher experimental results of IFT. Our simulation results are consistent with other results, indicating that our simulation model and method are reasonable and feasible for further researches.

**Table S2.** Simulated and actual densities of the water and decane bulk phase under different conditions.

<table>
<thead>
<tr>
<th>Conditions (K, atm)</th>
<th>Actual density (g·cm⁻³)</th>
<th>Our results (g·cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300, 1</td>
<td>0.997</td>
<td>0.998</td>
</tr>
<tr>
<td>320, 1</td>
<td>0.992</td>
<td>0.996</td>
</tr>
<tr>
<td>340, 1</td>
<td>0.989</td>
<td>0.991</td>
</tr>
<tr>
<td>300, 20</td>
<td>1.001</td>
<td>0.999</td>
</tr>
<tr>
<td>300, 40</td>
<td>1.002</td>
<td>1.001</td>
</tr>
<tr>
<td>Decane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300, 1</td>
<td>0.725</td>
<td>0.723</td>
</tr>
<tr>
<td>320, 1</td>
<td>0.710</td>
<td>0.712</td>
</tr>
<tr>
<td>340, 1</td>
<td>0.694</td>
<td>0.697</td>
</tr>
<tr>
<td>300, 20</td>
<td>0.726</td>
<td>0.723</td>
</tr>
<tr>
<td>300, 40</td>
<td>0.728</td>
<td>0.729</td>
</tr>
</tbody>
</table>

**Figure S1.** The IFT of the decane-water interface compared with the results of literatures (There is a slight difference for temperature, pressure and ion concentration).⁴⁻¹¹

**Table S3.** The comparison of simulated IFTs with the experimental results in the literatures under high pressure or temperature conditions (For the sake of contrastive analysis, we only listed the experimental results of the conditions which close to our simulated conditions).
<table>
<thead>
<tr>
<th>Authors et al.</th>
<th>year</th>
<th>IFT (mN/m)</th>
<th>T (K)</th>
<th>P (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Susnar\textsuperscript{12}</td>
<td>1994</td>
<td>51.64</td>
<td>294.65</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>51.7</td>
<td>294.35</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>51.79</td>
<td>294.35</td>
<td>35</td>
</tr>
<tr>
<td>Georgiadis\textsuperscript{13}</td>
<td>2011</td>
<td>51.96</td>
<td>297.85</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>47.78</td>
<td>323.35</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>46.28</td>
<td>343.45</td>
<td>1.5</td>
</tr>
<tr>
<td>Cai\textsuperscript{14}</td>
<td>1996</td>
<td>51.51</td>
<td>298.15</td>
<td>43.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>49</td>
<td>323.15</td>
<td>38.7</td>
</tr>
<tr>
<td>Wiegand\textsuperscript{15}</td>
<td>1994</td>
<td>51.1</td>
<td>295</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>44.38</td>
<td>353</td>
<td>1</td>
</tr>
<tr>
<td>Zeppieri\textsuperscript{16}</td>
<td>2001</td>
<td>51.98</td>
<td>298.15</td>
<td>1</td>
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<td></td>
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<td>51.77</td>
<td>300.65</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50.13</td>
<td>318.15</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>49.78</td>
<td>323.15</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>49.21</td>
<td>333.15</td>
<td>1</td>
</tr>
<tr>
<td>Our simulated results</td>
<td>2017</td>
<td>44.34</td>
<td>300</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>43.65</td>
<td>320</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>41.72</td>
<td>340</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>42.21</td>
<td>340</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>41.91</td>
<td>340</td>
<td>20</td>
</tr>
</tbody>
</table>

2. Interfacial structure

2.1 Interfacial thickness

As previously stated, we can obtain the interfacial thickness of the decane-water interface systems with different ion concentrations (300 K, 1 atm), as shown in Fig. S2. With ion concentration increasing, the interfacial thickness decreases firstly, and then increases. At the ion concentration of 0.9 mol/L, the thickness reaches a minimum. This trend agrees with the results of IFT (see Fig. 4(b)). The greater IFT means the stronger immiscibility, thus the lower interfacial thickness.
2.2 Adsorption of ions

According to the referenced studies\textsuperscript{11}, some kinds of ions can be adsorbed at or near the interface. Fig. S3 shows the number density distribution of sodium and chloride ions near the interface. It can be seen that the chloride ions have the stronger affinity toward the interface than the sodium ions because of their weaker hydration, which will be discussed in section 3.2. The slight fluctuations of curves may be because the simulation time is not long enough or the ionic hydration hinders the motion of ions.

3. Radial distribution function and ionic hydration
3.1 Radial distribution function

Fig. S4 shows the radial distribution function $g(r)$ of Na-Cl versus ion concentration. The fluctuations of curves may be because the simulation time is not long enough or the ionic hydration hinders the motion of ions. With ion concentration increasing, the distance $r$ where the first peak occurs reduces, indicating that the sodium and chloride ions are gradually close to each other. It is noteworthy that the distance $r$ where the first peak occurs at ion concentration of 1.5 mol/L is quite small and the peak value of $g_{Na-Cl}(r)$ is extremely higher than the other concentrations. The possible reason is that sodium and chloride ions are bound and exist in the water phase with the form of ion pair.

![Radial distribution function of Na-Cl in the decane-water systems with different ion concentrations.](image)

**Figure S4.** Radial distribution function of Na-Cl in the decane-water systems with different ion concentrations.

3.2 Hydration of ions

As we can see from Fig. S5, the decane molecules are likely to arrange themselves with carbon chain parallel to the interface and the dipole moment of water molecules also has the tendency to become parallel to the interface. The hydration of ions at or near the interface causes the aggregation of water molecules near ions, as shown in the right figure of Fig. S5. The number of hydrogen bond is greater for chloride ions than that for sodium ions because of their different hydrated structures. The oxygen atom of water in the first hydration layer of chloride ions is exposed to the water phase and has greater possibility to form hydrogen bond with other water molecules.
Figure S5. The conformation of decane (left), ions and water molecules (right) at or near the interface. (Purple: Decane molecules; Blue: Sodium ions; Brown: Chloride ions. The blue dashed line in the right figure represents the hydrogen bond)

The variations of ionic hydration at the interface under different ion concentrations are shown in Fig. S6. We can find that with the increase of ion concentration, more and more ions, particularly chloride ions, are adsorbed at the interface. From the enlarged view of the ionic hydrations, we can qualitatively conclude that the hydration of sodium ions is stronger than the hydration of chloride ions, which is quantitatively described in the section of **Hydration of ions** in the manuscript. At high ion concentrations (1.5 mol/L), the ions at the interface are close to one another owing to the more ions at the interface. A few oppositely charged ions can even bind together in the form of ion pair, as shown in the right map of Fig. S6. In terms of the significant effect of ion-pairs on IFT, we further calculate the number of ion-pairs at the interface (see Table S3). We find that the number of ion-pairs at the interface increases with ion concentration increasing. Particularly, a significant rise of the number of ion-pairs occurs at high ion concentrations (> 0.9 mol/L), which plays an important role in the decrease of IFT.
**Table S4.** Number of ion-pair at the interface for the decane-water system with different ion concentrations (300K, 1 atm).

<table>
<thead>
<tr>
<th>Ion concentration (mol/L)</th>
<th>0.3</th>
<th>0.6</th>
<th>0.9</th>
<th>1.2</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average number of ion-pair for every frame</td>
<td>0.028</td>
<td>0.431</td>
<td>0.643</td>
<td>1.960</td>
<td>2.926</td>
</tr>
</tbody>
</table>

For the sake of comparison, we run MD simulations with only one ion (sodium or chloride) at the interface. As we can see from Figure S7, the z-coordinate of ion fluctuates between the interface and the bulk phase, showing that the behavior of ion at the interface is a dynamic process including the adsorption, desorption and diffusion at the interface, as shown in illustration of Figure S7 shown. For different ions with different hydration abilities, the residence time at the interface are different; namely, the sodium ion is strongly surrounded by water molecules and therefore stays at the interface for a short time while the chloride ion has the opposite trend. Since the residence time of ion at the interface is shorter than that in the bulk and the interaction between single ion and the interface is very weak, the time-averaged value (such as interfacial tension) in the simulations is almost the same as that of the decane-water interface without ions. Meanwhile, single ion at the interface cannot reflect the interactions between ions. Thus, the decane-water
interface without ions can serve as a reference to reveal the effects of interaction between ions on the interface tension and it is not necessarily to study the single ion at the interface.

**Figure S7.** The z-coordinate distribution of single ion versus simulation time.
References