ABSTRACT

Alcohols, including branched and straight ones, have been used extensively in industrial processes to enhance the interface effect. Amongst these, methyl isobutyl carbinol (MIBC) is particularly popular due to the superior performance in mineral flotation. The interfacial behavior of MIBC at the air/liquid interface has been investigated employing foaminess, thin aqueous film and zeta-potential. Recently, the surface potential (AV), which is a fundamental factor influencing the double-layer force and disjoining pressure, was investigated by ionizing 241 Am electrode. In this study, molecular dynamics (MD) simulation was employed to calculate the surface tension and surface potential of MIBC at different surface concentrations. The simulation results were consistent with experimental data. The study highlights the significant role of interaction between water and alcohol molecules at the interface, which is often overlooked by conventional theory.

Keywords: molecular dynamics simulation, air/liquid interface, surface potential, MIBC

INTRODUCTION

The behavior of alcohol at the adsorption layer at an air/water interface can dramatically change the interfacial properties and significantly affect industrial processes such as mineral flotation (Klimpel and Isherwood, 1991) and steam condensation (Jun et al., 2010). For instance, the adsorption of alcohols at the air/water interface of foam film (Kararakashev et al., 2007) can significantly stabilize foams, which is widely applied in chemical processes. For mineral flotation, MIBC has been proved superior over other hexanol isomers as flotation frother (Klimpel and Isherwood, 1991). However, MIBC is very flammable and has caused some serious accidents within the industry.

Recently, the influence of MIBC adsorption on the air/water interfacial potential was quantified (Phan et al., 2012), which is particularly important for double-layer charge and critically affects the disjoining pressure, thin film stabilizing and foaminess (Wang and Yoon, 2008). Despite negative charge on hydrophilic group, MIBC has a positive effect on surface potential and the interaction between adsorbed MIBC and surrounding water molecules is complicated. To quantify the advantages of MIBC over other isomers (e.g. 1-hexanol), one would need to investigate the interfacial phenomena at the molecular scale.

Over the last few decades, molecular dynamics (MD) simulation has become a common tool in theoretical studies both of simple liquids and large bio-molecular systems such as proteins or DNA in a realistic solvent environment. In this study, the influence of MIBC on the air/water surface potential and surface tension were investigated by molecular dynamics. Consequently, the results were compared with experimental data and the analytical prediction to provide new insights into the phenomena.
EXPERIMENT METHOD

Surface tension measurement
The experimental set up consisted of Wilhelmy plate method (Barnes, 2005), using tensiometer KSV Sigma 701 (KSV Instrument Ltd., Finland) cooperated with an automatic micro-disperser (Phan et al., 2012).

Surface potential ($\Delta V$) measurement
The surface potential of the MIBC solutions was determined relative to the surface potential of the pure supporting electrolyte using ionizing Am electrode. Details of surface potential measurement have been described elsewhere (Nakahara et al., 2011).

SIMULATION METHOD

The air-liquid interface was simulated using the simulation box constructed with a slab of water layer (around 10 nm thickness) placed between two empty regions (10 nm each) as shown in Fig.1.

Fig. 1: Simulation: (a) molecular structure of MIBC under investigation, (b) simulation box (red: water, blue: MIBC)

The simulations were performed at the constant temperature ($T = 298.15 \text{ K}$) and volume in an orthorhombic simulation cell of $3 \text{ nm} \times 3 \text{ nm} \times 10 \text{ nm}$, which was the same as a previous study in the literature (Vega and de Miguel, 2007). The GROMACS version 4.5.5 (Hess et al., 2008) was used to generate the molecular trajectories using a time step of 1fs. In this study, the most popular water model SPC/E, Simple Point Charge-Extended, (Chen, 2007) and standard ions ($\text{Na}^+$, $\text{Cl}^-$) parameters in GROMACS 4.5.5 was employed. In order to simulate MIBC molecules at the air-liquid interface, the different numbers (4, 6, 8, 12, 14, 16, 18 and 20) of MIBCs were placed at both interfaces before filling up the cell with water. Then 214 water molecules were replaced by 107 $\text{Na}^+$ 107 $\text{Cl}^-$ ions (which correspond to a concentration of 2M). A simulation without MIBCs was also performed to provide the reference system.

The first step is to keep the temperature constant at 298.15 K by using a Nose-Hoover thermostat with a relaxation time of 2 ps and cut-off of 1.3 nm. Then the cell length ($z$ direction) was increased to 30 nm before running for 20 ns for data analysis. The average of surface tension during last 2 ns was extracted and used as equilibrium surface tension. Ewald sums were used to deal with the electrostatic interactions. The surface tension, distributions of MIBC, water, ions and surface potential were obtained by analyzing the trajectories recorded at every 500 fs.

The molecular potential for MIBC was obtained from PRODRG (Schuttelkopf, 2004) using GROMOS87 force-field. United model was used: all hydrogen atoms, except H in hydroxyl
group, were united with the corresponding carbon. The first run using unadjusted molecular potential was not successful: the MIBC molecules kept moving out of the water layer into the vacuum area. In this instance, the hydrophilic force introduced by the dipole moment of hydroxyl group was not strong enough to overcome the hydrophobic nature of alkyl group.

Consequently, the charge distribution was adjusted using the proposed distribution in the literature (Jorgensen, 1986): partial charges are designated to hydroxyl group (O: -0.700, H: 0.435) and alpha-C (C: 0.265), whereas all atoms in the alkyl group are neutrally charged (Table 1).

Table 1. Charge distributions for MIBC

<table>
<thead>
<tr>
<th>United Atom</th>
<th>Mass</th>
<th>PRODRG charge</th>
<th>Modified charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3</td>
<td>15.0350</td>
<td>-0.015</td>
<td>0</td>
</tr>
<tr>
<td>CH</td>
<td>13.0190</td>
<td>0.031</td>
<td>0</td>
</tr>
<tr>
<td>CH3</td>
<td>15.0350</td>
<td>-0.016</td>
<td>0</td>
</tr>
<tr>
<td>CH2</td>
<td>14.0270</td>
<td>0.040</td>
<td>0</td>
</tr>
<tr>
<td>CH</td>
<td>13.0190</td>
<td>0.119</td>
<td>0.265</td>
</tr>
<tr>
<td>CH3</td>
<td>15.0350</td>
<td>-0.004</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>15.9994</td>
<td>-0.175</td>
<td>-0.700</td>
</tr>
<tr>
<td>H</td>
<td>1.0080</td>
<td>0.020</td>
<td>0.435</td>
</tr>
</tbody>
</table>

RESULT AND DISCUSSION

Density distribution

![Density distribution](image)

Fig. 2: Density distribution of simulation box with 8 MIBCs on each side

The average density distribution was calculated for water, MIBC, Na⁺ and Cl⁻. From Fig. 2, it can be seen that MIBCs were clearly distributed around the air-water interface and hence the MIBCs represented the surface concentration not bulk concentration. There was no interaction between MIBCs from the two opposite sides. Consequently, the potential of water layer represents the bulk property of solution. The density of Na⁺ and Cl⁻ at the air/water interface are relatively small, which is consistent to the negative adsorption.

The density profile of water, \( \rho(z) \), was determined by fitting the simulation data with an error function of the following form (Yuet and Blankschtein, 2010, Senapati and Berkowitz, 2001):
\[
\rho(z) = \frac{\rho_0}{2} \left( 1 - \text{erf} \left( \frac{z - z_0}{\sqrt{2}w} \right) \right)
\]

where \(\rho_0\) is the water density, \(z_0\) is the midpoint of the interface, or the location of the Gibbs dividing plane (GDP), and \(w\) is the width of the interface due to thermal fluctuations of this interface. Solver (in MS Excel) was employed to determine the location of GDP as well as the thickness of interfacial zone.

Table 2. Simulated water density (\(\rho_0\)), location of GDP (\(z_0\)), and the width of the interface (\(w\))

<table>
<thead>
<tr>
<th>MIBC</th>
<th>(\rho_0) (kg/m³)</th>
<th>(z_0) (nm)</th>
<th>(w) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>964.00</td>
<td>10.039</td>
<td>0.299</td>
</tr>
<tr>
<td>4</td>
<td>950.41</td>
<td>10.093</td>
<td>0.313</td>
</tr>
<tr>
<td>6</td>
<td>966.79</td>
<td>10.171</td>
<td>0.339</td>
</tr>
<tr>
<td>8</td>
<td>961.63</td>
<td>10.176</td>
<td>0.336</td>
</tr>
<tr>
<td>12</td>
<td>969.33</td>
<td>10.239</td>
<td>0.364</td>
</tr>
<tr>
<td>14</td>
<td>965.93</td>
<td>10.306</td>
<td>0.367</td>
</tr>
<tr>
<td>16</td>
<td>954.47</td>
<td>10.401</td>
<td>0.359</td>
</tr>
<tr>
<td>18</td>
<td>964.38</td>
<td>10.484</td>
<td>0.373</td>
</tr>
<tr>
<td>20</td>
<td>963.93</td>
<td>10.494</td>
<td>0.370</td>
</tr>
</tbody>
</table>

It is shown in Table 2 that GDP was located further into the bulk with the increasing surface excess (number of MIBCs). Moreover, additional MIBC molecules also make the interface thicker, which contributes to the reduction in interfacial tension (Petersen, 2006) and is consistent to the result of surface tension calculations mentioned below.

![Fig. 3: The density of water, hydrophobic tail and hydrophilic head. Location of Gibbs dividing plane and the width of water interface (8 MIBCs each side)](image)

The average density distribution for hydrophobic tail (carbon chain) and hydrophilic head (hydroxyl) were also calculated separately. In this study, the “head” is the-OH group. On the other hand, the “tail” consists of the carbon chain.

The density profiles of the head and tail groups were found by fitting the simulation data with the Gaussian distribution:
\[ \rho_i(z) = \rho_i^0 \exp \left[ -\frac{4(z - z_i^0)^2}{\sigma_i^2} \right] \]  

where \( i \) is \( t \) (tail) or \( h \) (head), \( \sigma_i \) is the width of the distribution, \( z_i^0 \) is the center and \( \rho_i^0 \) is density at center, respectively.

In Fig.3, the dotted lines are perpendicular to the \( z \)-axis and indicate the \( z \)-position of the dividing plane, centers of the “head” and “tail”. The values of \( \sigma, \rho_i^0 \), \( D_1 \) and \( D_2 \) (distance from carbon tail and –OH head group to the GDP, respectively) were obtained by Solver and are tabulated in Table 3.

Table. 3: Relative distances between hydrophobic and hydrophilic groups.

<table>
<thead>
<tr>
<th>MIBCs</th>
<th>( D_1 ) (nm)</th>
<th>( D_2 ) (nm)</th>
<th>( D ) (nm)</th>
<th>( \sigma ) (nm)</th>
<th>( \sigma_i ) (nm)</th>
<th>( \rho_i^0 ) (kg/m(^3))</th>
<th>( \rho_i^0 ) (kg/m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.112</td>
<td>0.061</td>
<td>0.173</td>
<td>0.437</td>
<td>0.373</td>
<td>163.51</td>
<td>38.44</td>
</tr>
<tr>
<td>6</td>
<td>0.124</td>
<td>0.050</td>
<td>0.174</td>
<td>0.442</td>
<td>0.369</td>
<td>239.92</td>
<td>57.60</td>
</tr>
<tr>
<td>8</td>
<td>0.144</td>
<td>0.031</td>
<td>0.175</td>
<td>0.451</td>
<td>0.376</td>
<td>317.44</td>
<td>76.12</td>
</tr>
<tr>
<td>12</td>
<td>0.172</td>
<td>0.005</td>
<td>0.177</td>
<td>0.475</td>
<td>0.391</td>
<td>454.39</td>
<td>110.51</td>
</tr>
<tr>
<td>14</td>
<td>0.187</td>
<td>-0.010</td>
<td>0.177</td>
<td>0.476</td>
<td>0.388</td>
<td>529.54</td>
<td>129.76</td>
</tr>
<tr>
<td>16</td>
<td>0.205</td>
<td>-0.025</td>
<td>0.180</td>
<td>0.489</td>
<td>0.398</td>
<td>589.73</td>
<td>144.71</td>
</tr>
<tr>
<td>18</td>
<td>0.235</td>
<td>-0.058</td>
<td>0.177</td>
<td>0.528</td>
<td>0.423</td>
<td>679.26</td>
<td>169.02</td>
</tr>
<tr>
<td>20</td>
<td>0.234</td>
<td>-0.058</td>
<td>0.176</td>
<td>0.531</td>
<td>0.432</td>
<td>676.08</td>
<td>169.02</td>
</tr>
</tbody>
</table>

It is clear from the Table 3 that MIBCs moved further into the vapor phase (from the dividing plane) with increasing numbers of MIBCs. This indicates a strong interaction between the head groups and water molecules at the interface. At high concentrations, the MIBC molecules are mostly located outside the Gibbs dividing plane. Whereas, \( \sigma \) and \( \rho_i^0 \) increase linearly with MIBCs concentration as expected.

**Surface tension**

Surface tension and surface potential were calculated by functions supplied with GROMACS. The surface tension \( \gamma(t) \) was calculated from the pressure tensor:

\[
\gamma(t) = \frac{1}{2L_z} \int_0^L \left[ P_{xx}(z,t) - \frac{P_{xx}(z,t) + P_{yy}(z,t)}{2} \right] dz
\]

where \( L_z \) is the length of the box, \( P_{xx}, P_{yy}, P_{zz} \) are the three diagonal components of the pressure tensor along the \( x \)-, \( y \)-, and \( z \)-direction, respectively.

Subsequently, accumulated average of surface tension was obtained and plotted as function of time. The pure water surface tension was measured at 60.1mN/m, which is similar to literature values for SPC/E: 61.9 (Chen, 2007), 63.6 (Vega and de Miguel, 2007), and 60.7mN/m (Yuet and Blankschtein, 2010). In presence of 2M NaCl, the surface tension was calculated at 60.5 mN/m, which is consistent with experiment (it is well-known that NaCl increases surface tension of water slightly).
For MIBC/NaCl in water simulations, the surface tension was very distinguishable (Fig 4) and can be compared to theoretical prediction (Fig. 5). The theoretical prediction in Fig. 5 was generated from Langmuir isotherm:

\[
\Gamma - \Gamma = \frac{a m}{a b} K c_1 \quad [4]
\]

where \(a \Gamma\) is surfactant excess, \(m \Gamma\) is saturated surface excess and \(K\) is the surface affinity.

The two adsorption constants, \(K\) and \(m \Gamma\), were found by fitting surface tension to the Szyszkowski equation (Chang and Franses, 1995):

\[
\gamma_0 - \gamma_a = -RTm \ln(1 - Kc_b) \quad [5]
\]

where \(\gamma_0\) and \(\gamma_a\) are surface tension of alcohol-free (supporting solute) and alcohol solutions.

From previous study, the best-fitted \(K\) and \(m \Gamma\) for MIBC with 2M NaCl solution were found at 369.0 M\(^{-1}\) and 6.36\( \times \) 10\(^{-6}\) mol/m\(^2\), respectively (Phan et al., 2012).
In Fig. 5, it is clear that the surface tension of the system decreased with increasing MIBCs and followed the experimental trend qualitatively. The simulated data fits theoretical prediction well (with $R^2 = 0.9329$) if adjusted by $\Delta\gamma_0$, which is the difference between simulated and experimental surface tension of NaCl solution. In other words, the simulated surface pressure, $\pi = \gamma_0 - \gamma_a$, matches experimental values without further fitting.

For our system, $\Delta\gamma_0$ equals to 14.83 mN/m, which accounts for the limitations of water model and the simulations parameters. The variation in surface tension can be contributed to water models, simulation size (box dimension), running time and cut-off radius. These factors are being discussed in the literature with various results from different groups (Yuet and Blankschtein, 2010, Mountain, 2009, Vega and de Miguel, 2007, Chen, 2007).

**Surface Potential**

The surface potential was obtained for the production run using the following formula:

$$\psi(z) - \psi(0) = -\int_0^z dz' \int_0^{z'} \frac{\rho_c(z')}{\varepsilon_0} dz''$$  \hspace{1cm} [6]$$

where $\varepsilon_0$ is the vacuum permittivity.
Pure water has negative potential (-578 mV), which is reasonable with previous results in the literature, -546 mV (Kathmann et al., 2008). Moving inside the liquid phase, water molecules are randomly oriented and thus the potential changes insignificantly.

For MIBC in NaCl solution, the potential of MIBC and combined ions/water were obtained separately. Fig. 6 shows that MIBCs generated a negative potential at the interface. This is expectable from the charge distribution between alpha-carbon and oxygen in Table 1. However, MIBCs increased the total potential of ions and water, i.e. less negative in comparison to ions/water system. This effect clearly demonstrates the disorientation of water molecules by adsorbed MIBCs as proposed theoretically (Phan et al., 2012).

On the other hand, the total surface potential (i.e. MIBCs + ions + water), is more negative than that of ions and water. This is contradictory to experiment data, which shown a positive influence of MIBCs on surface potential. One of the reasons for this discrepancy is the over-simplification of MIBC molecular charge distribution. For instance, the hydrocarbon chain of MIBC could have more complicated charge and some carbon-carbon bonds may contribute positively on overall potential. Moreover, the charge distribution of MIBC in Table 1 could over-estimate the dipole moment of MIBC. It is also noteworthy that water models could significantly influence surface potential as well (Kathmann et al., 2011).

In order to verify the model results, the experiment data was combined with theoretical analysis to predict the surface potential of MIBC in NaCl solution (at 2M). From previous study, the surface potential of MIBC in electrolyte solution is given by the following equation (Phan et al., 2012):

\[
\Delta V = N_A \Gamma_a \frac{\mu'}{\varepsilon_a \varepsilon_0} + \sigma \frac{\lambda_s}{\varepsilon_s \varepsilon_0} + \Psi_d \tag{7}
\]

where \(N_A\) is Avogadro number, \(\varepsilon_0\) is dielectric permittivity of absorbed layer, \(\varepsilon_a\) and \(\varepsilon_s\) are dielectric permittivity of adsorbed layer and stern layer respectively, \(\mu'\) is the total normal dipole moment per MIBC molecules, \(\Psi_d\) is the potential at the limit of the diffuse layer.
The total normal dipole moment per MIBC molecules ($\mu'$) consists of two components: (i) dipole moment of absorbed alcohol and (ii) dipole moment of water molecules disordered by alcohols (Nakahara et al., 2008). Hence, it can be assumed that the ratio between these two components is constant for the range of concentration under investigation. In the other words, the number of disordered water molecules is proportional to the number of absorbed MIBCs. It should be noted that this relationship might not hold for higher MIBC concentration, when a water molecule can be disordered by two or more MIBCs at the same time.

The best-fitted values of parameters were identified previously (Phan et al., 2012) and used to predict the surface potential of MIBC/NaCl solution. It can be seen clearly that the potential of ions/water increased in relation to the increase in MIBC surface excess and considerably higher than the theoretical prediction.

![Comparison with theoretical prediction data](image)

**Fig. 7:** Surface potential as function of MIBC surface excess (line: theoretical prediction; points: simulated data).

**Comparison with theoretical prediction data**

The simulated results were fitted quantitatively with theoretical prediction by two different ways. In the first method, an empirical parameter, $k$, was introduced to fit the simulated results of ions/water to the prediction:

$$\Delta V = k \Delta V_{ion+water}$$  \[8\]

where $\Delta V_{ion+water}$ is the total potential of ions and water.

Alternatively, another parameter, $l$, was introduced:

$$\Delta V = \Delta V_{ion+water} + l \Delta V_{MIBC}$$  \[9\]

where $\Delta V_{MIBC}$ is the potential of MIBCs.

Using linear regression, the best-fitted value of $l$ and $k$ were determined at 0.285 and 0.459, respectively. From Fig. 7, it can be seen that both methods provided an adequate fitting.
DISCUSSION

The simulations show that MIBCs change both surface tension (decreasing) and surface potential (increasing) of water as predicted by experimental data. The simulated surface tensions were comparable to experimental data. While the simulation did not fit the surface potential without an additional empirical parameter, the results can provide new insights into the interaction between water and MIBCs at the interface zone. The results confirm the two components in surface potential (\(\mu'\)): (i) dipole moment of adsorbed alcohols and (ii) dipole moment of water molecules disordered by alcohols (Warszyński et al., 1998, Nakahara et al., 2008).

The best-fitted value, \(l=0.285\), explains the overall positive influence of MIBCs on surface potential of the system despite of the negative potential themselves. Moreover, the best-fitted value of \(k, k<1\), indicated that water molecules over-presented the dipole moments at the interface. Qualitatively, the disturbed water molecules (component ii) have higher contribution to changes in surface properties than the MIBCs themselves (component i). The arrangement of water molecules verified the disturbance caused by the presence of MIBC molecules.

It should be noted that the current theoretical analysis focus on adsorbed concentration and interactions between adsorbed surfactants only. Theoretically, the Gibbs isotherm can be used to relate the adsorbed surfactants to reduction in surface tension. In the current theoretical framework (Prosser and Franses, 2001), the interaction between water molecules and surfactants are not included. Moreover, the contribution of water molecules on the surface tension is not accounted for. The results from this study clearly showing the significance of behavior of these water molecules on the physical properties of the system.

CONCLUSIONS

The study successfully demonstrated the applicability of molecular dynamics to describe the systems of MIBC in aqueous NaCl solutions in terms of density, surface tension and surface potential. The simulations highlighted the distribution between “head” and “tail” of MIBC molecules at the interface, the change in tension and potential with varying concentrations the air/water interface. The surface pressure (the change in surface tension) compared very well with experimental data. On the other hand, the surface potential results required a fitting parameter, either \(l\) or \(k\). The result highlighted the interactions between MIBCs and water in the air/water interface layer, which is often neglected in the literature.

The application of molecular dynamics is also critical to understand the interface structure and the influence of molecular structure (for instance between MIBC, 1-hexanol and 2-hexanol) on the microscopic properties of interfaces. Further complimentary investigations with different alcohols are being conducted to provide insights into the interactions between adsorbed surfactants and water on the properties of interfaces.

REFERENCES


