Atomistic Insights into Hydrogen-Bonding Driven Competitive Adsorption of Acetone-Chloroform Binary Mixtures

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Figure S1. Total atomic (solid red line) and center of mass (dashed black line) densities of an a) acetone and a b) chloroform film on an OH-terminated sapphire substrate along the surface normal i.e. axis perpendicular to the substrate. Three and two solid lines for acetone and chloroform, respectively, represent the depletion points relevant for layering. The lines define three (0-4.6 Å, 4.6-8.8 Å, and 8.8-13.0 Å) and two (0-5 Å and 5-9 Å) layers for acetone and chloroform, respectively.
Figure S2. Normalized atomic densities of a chloroform film on an OH-terminated sapphire substrate along the surface normal i.e. axis perpendicular to the substrate. Normalization is done with respect to the bulk atomic densities of the individual component to itself.

Figure S3. a) Orientation distributions of the carbonyl bond vector (C=O) of acetone in a 4.0 Å thick layer (open red squares), 4.5 Å thick layer (solid blue upward triangles), and 5.0 Å thick layer (open black circles). b) Orientation distributions of the C-H bond vector of chloroform in a 4.5 Å thick layer (open red squares), 5.0 Å thick layer (solid blue upward triangles), and 5.5 Å thick layer (open black circles). The orientation distributions for different thickness of first layer have been plotted to check the sensitivity of the peak at cosθ = 1 to the interfacial layer thickness. All the orientation distributions are with respect to the z-direction and expressed as probability distribution of cosine of the tilt angle (θ) depicted pictorially. All-atom representation with CPK coloring has been selected for visualization of acetone and chloroform molecules.
Figure S4. Total mass density of pure acetone (red solid line), pure chloroform (black dashed line), 5:95 (acetone:chloroform) binary mixture (orange dashed-dotted line), and 50:50 (acetone:chloroform) binary mixture (dark green dotted line) film on an OH-terminated sapphire substrate along the surface normal i.e. axis perpendicular to the substrate.

Figure S5. Atomic densities of a) 5:95 and b) 50:50 (acetone:chloroform) binary mixtures on an OH-terminated sapphire substrate along the surface normal i.e. axis perpendicular to the substrate. Total atomic density profile for the two binary mixtures are shown by the black solid line. The atomic density for hydrogen is very small in magnitude.
Table S1. Raw counts of acetone and chloroform molecules using the Z-cut and radial-cut methods for last 300 frames.

<table>
<thead>
<tr>
<th>Mole Ratio (Acetone: Chloroform)</th>
<th>Number of Acetone Molecules within Z-cut</th>
<th>Number of Acetone Molecules within radial-cut</th>
<th>Number of Chloroform Molecules within Z-cut</th>
<th>Number of Chloroform Molecules within radial-cut</th>
<th>Surface Segregation of Acetone (Z-cut)</th>
<th>Surface Segregation of Acetone (Radial-cut)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.98</td>
<td>4793</td>
<td>1676</td>
<td>22881</td>
<td>2813</td>
<td>0.1732</td>
<td>0.3733</td>
</tr>
<tr>
<td>5.95</td>
<td>7036</td>
<td>3760</td>
<td>20736</td>
<td>2090</td>
<td>0.2534</td>
<td>0.6427</td>
</tr>
<tr>
<td>10.90</td>
<td>9751</td>
<td>5170</td>
<td>18138</td>
<td>1270</td>
<td>0.3496</td>
<td>0.8028</td>
</tr>
<tr>
<td>25.75</td>
<td>13920</td>
<td>5455</td>
<td>14313</td>
<td>415</td>
<td>0.4930</td>
<td>0.9293</td>
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<tr>
<td>50.50</td>
<td>18679</td>
<td>8180</td>
<td>9916</td>
<td>280</td>
<td>0.6533</td>
<td>0.9669</td>
</tr>
</tbody>
</table>

Section S1. Sapphire Hydroxyl Group Orientation

In this section, the orientation distribution of the sapphire surface hydroxyl groups and surface adsorbed molecules were studied to gain insights into the adsorption process and experimental assumptions. Two underlying assumptions were employed in the experimental quantification of surface segregation.\(^1\) The first was that the orientation distribution of the sapphire surface hydroxyl groups remains constant as a function of bulk concentration. The second was that the presence of the second liquid does not affect the shape of the hydroxyl peak compared to the pure solvent case.

![Figure S6. Orientation distribution of -OH bond vector of sapphire with respect to the surface normal in four different environments: pure acetone (red solid circles-solid line), pure chloroform (black solid squares-dashed line), 5:95 (acetone:chloroform) binary mixture (orange open hexagons-dashed dotted line), and 50:50 (acetone:chloroform) binary mixture (dark green open triangles-dotted line).](image_url)

The orientation distribution obtained from the simulation of the sapphire surface hydroxyl groups can potentially influence the surface segregation result, since orientations could affect the interactions between the sapphire and the adsorbed molecules. Figure S6 shows the orientation distribution of sapphire surface hydroxyl groups for pure liquids (acetone and chloroform) and liquid mixtures (5:95 and 50:50). Even though a comparison of the orientation...
distribution of hydroxyl groups in the pure cases shows slight differences, the profile for the binary mixture with only 5 mol % acetone closely matches the pure acetone case. This observation agrees with a model for preferential surface segregation of acetone over chloroform. The relative insensitivity of the hydroxyl orientation distribution supports the first experimental assumption that justifies the calculated surface segregation by Singla et al. from SFG amplitudes. In the work by Singla et al., the ratio of SFG amplitudes was used to calculate the interfacial area fractions in order to quantify the competitive adsorption of molecules. Since the effect of the orientation distribution cancels out in the calculation of the interfacial area fraction as given by equation S2 in the supporting information for their manuscript, the SFG amplitude could be used as a direct measure of surface concentration.

In the past, for analyzing SFG data in the hydrocarbon region, it was assumed that the molecular orientation does not change as a function of bulk composition. Additionally, the second conjecture in the experimental study by Singla et al. was that the shape of the sapphire hydroxyl peak does not change across bulk concentrations. The spectral line-shape of hydroxyl band is representative of the interaction energy distribution and may be related to the orientation distribution of adsorbed molecules (discussed in section 3.1, main manuscript), so understanding the effect of orientation can help clarify the experimental analysis. Since the orientation of acetone and chloroform molecules changes as a function of bulk concentration, a rigorous analysis of SFG results should consider the changing orientation of molecules in order to calculate more accurate surface concentrations.
References

