Raman Characterization of Binary Hydrates

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Background

Clathrate hydrates are inclusion compounds composed of water molecules (“hosts”), which form a cage structure wherein other molecules (“guests”) may be trapped. Their applications range from gas separation to desalination.

Binary hydrates have two different guests occupying the same structure. Although cyclopentane (CP) hydrates and tetrahydrofuran (THF) hydrates have both been studied in depth, the combination of these guests in a binary hydrate has not yet been investigated.

Objectives

• Form binary hydrates with a combination of CP and THF as guests
• Obtain a Raman spectroscopic footprint of these binary hydrates

Methods

1. Cool 10 g of the desired guest for ~1 hour at 0 - 7.7°C.
2. Add 2 g of ice particles (~50 µm)
3. Store mixture for ~8 hours at 0 - 7.7°C.
4. Remove solids and analyze using Raman spectroscopy and differential scanning calorimetry (DSC). During Raman analysis, preserve hydrate samples using a cooling stage.

Table 1: Raman peaks of various substances in this study

<table>
<thead>
<tr>
<th>Substance</th>
<th>Expt (cm⁻¹)</th>
<th>Lit [2] (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP Liquid</td>
<td>887 1029.2</td>
<td>889 1030</td>
</tr>
<tr>
<td>CP Hydrate</td>
<td>896 1033.8</td>
<td>896</td>
</tr>
<tr>
<td>25 wt% THF + 75 wt% CP Hydrate</td>
<td>884.6 ~917 1029.6</td>
<td>~885 918.1 1031.7</td>
</tr>
<tr>
<td>50 wt% THF + 50 wt% CP Hydrate</td>
<td>~885 916.5 1031.7</td>
<td>-</td>
</tr>
<tr>
<td>75 wt% THF + 25 wt% CP Hydrate</td>
<td>~885 916.5 1031.7</td>
<td>-</td>
</tr>
<tr>
<td>THF Hydrate</td>
<td>926.7 1037.3</td>
<td>920 1034</td>
</tr>
<tr>
<td>THF Liquid</td>
<td>912.9 1029.6</td>
<td>914 1030</td>
</tr>
</tbody>
</table>

Results

Raman Spectra of THF + CP Hydrates

Fig. 1: CP and THF both form a type II hydrate structure (left [1]). CP/THF hydrate crystals from this work (right).

Table 1: Raman peaks of various substances in this study

Conclusions

• DSC data shows melting point higher than ice
• Indicates hydrate formation
• Raman peaks of CP + THF binary hydrate samples (~885, ~917) are different from the single hydrates
• 880-1100 peaks due to in-plane ring vibrations of guests in large hydrate cages

Future Work

• Characterize binary hydrates with X-Ray Diffraction
• Explore TBAB + CP binary hydrates

References


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