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Organic Lab 309:03  
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Experiment 16: Separation of an Alkane Clathrate

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**Purpose:**

To form a urea clathrate to separate alkanes.

**Equations:****Mechanisms:****Amounts and Properties:**

Table 1: Important Chemical Properties and Amounts

Chemicals	Mol Wt	BP	MP	D	$n_{\frac{20}{D}}$	Amounts
Hexadecane	226.4	287	18	.773	1.4345	10 mmol
2,2,4-trimethylpentane	114.2	99	-107	.692	1.3915	5 mL
Methanol	32.0	65	-98	.792	1.3292	50 mL
Urea	60.06		135	1.323		200 mmol

**Hazards and Safety:**

Both alkanes are flammable, no flames or hot surfaces near them. Methanol is flammable and harmful if ingested, inhaled, or absorbed through skin. Avoid contact with liquid and do not breathe vapors. DCM may be harmful if ingested, inhaled, or absorbed through skin, and prolonged inhalation can cause cancer. Dispose all chemicals in labeled containers within the hood.

**Procedure:****Reaction:**

1. Acquire 10 mmol of hexadecane and add 5 mL of 2,2,4-trimethylpentane.
2. Combine 200 mmol of urea and 50 mL methanol in 125 mL flask.
3. Warm the urea and methanol mixture to a temperature around 55 to 60 degrees Celsius with a stirring rod until all the urea is gone.
4. While solution is still warm, add the alkanes and use a small amount of methanol to transfer.

5. Stir or Swirl until a white solid begins to separate, and set the solution aside and let it cool slowly.
6. Cool in ice beaker for 10 minutes or more until crystallization is complete.

The first step is to create the mixture of alkanes to add to the urea and methanol solution that will be prepared in the next few steps. While adding the alkanes to the warm solution, the urea can form a clathrate with one of the alkanes, but specifically the hexadecane. This is due to urea being able to grasp on to a linear alkane better than a branched alkane. Cooling down the solution

### **Separation:**

1. Collect clathrate by vacuum filtration and wash with ice cold methanol.
2. Dry to mass at room temperature.
3. Weigh accurately.
4. Mix clathrate in 25 mL of warm water and stir water in steam bath or boiling water for several minutes.
5. Cool mixture in ice or water bath, and alkane may solidify while cooling.
6. Transfer mixture to separatory funnel using DCM as transfer and extract with two portions of DCM for the alkane part.
7. Dry combined extracts over anhydrous sodium sulfate.
8. After removing drying agent, evaporate the solvent completely using cold trap. Weigh guest alkane accurately.

After vacuum filtrating the clathrate, there will still be liquid within the clathrate, which requires drying before continuing with the experiment. Weighing accurately decreases the percent error of the experiment. When mixing the clathrate under warm water again, the clathrate can break up into the urea and alkane portions.

### **Analysis:**

1. Record infrared spectrum of guest alkane and use it to identify.  
Use IR to identify the guest alkane that was stuck with the urea to form the clathrate.

### **Observations:**

After beginning to create the clathrate, the solution became a cloudy substance that began to harden very rapidly. The solid that formed stopped the stir bar from stirring but after adding the heat, the solid began to redissolve. After redissolving

**Measurements:**

Table 2: Measurements during the experiment

12.026g urea used	50 mL Methanol used
2.260g hexadecane	5 mL 2,2,4-trimethylpentane
Mass of System: 48.030g	Mass after: 55.913g

**Data and Calculations:**

55.913g - 48.030g = 7.883g yielded

% yield:  $\frac{7.883\text{ g}}{2.260\text{ g}} * 100 = 348.9\% \text{ yield}$

**Discussions:**

Since there was a 348.9% yield, there was definitely impurities that went through to the end reaction. Surprisingly enough, even though there were a lot of impurities, The IR that was collected compared to the documented had a few distinct differences, but the peaks that were important to identify the hexadecane. Around the 2900 to 3000 region there are the three peaks in the documented IR which is extremely close to the IR that was collected. Near the 1500 region, the peaks in the documented IR also match up with the collected IR. In between these two regions, the peaks that are between them represent the impurities that had gone through. The impurities, however, did not resemble the peaks of the branched alkane which shows that the urea formed a clathrate between itself and the linear alkane.

**Conclusions:**

Due to the high percent yield, there could've been an error where the massing was done. The mass could've been from a state before the desired step to mass or there were other substances that were around the outside of the glass when massing. This high yield can also mean that the product after the rotovapping was still not completely drying, thus increasing the mass of the whole system. Since the important characteristic bands in the IR match with what the documented IR is, it can be said that the clathrate with urea had formed with a linear alkane better than that of a branched alkane.

**Exercises:**

1.  $1.5 + (.65n) = \text{guest/host ratio}$  Hexadecane has 16 carbons so  $n = 16$ . Plugging into the equation, it yields 11.9, which rounded up is 12.
2. At around the 1500 region, there are two large bands for 2,2,4-trimethylpentane. Compared to hexadecane, the 1500 region has just a small band. For the branched alkane, at the 2800 region, there is a broad flat peak compared to the hexadecane one with two peaks at the same region.

3. A. Putting octane in the isooctane bottle will make it so that a clathrate will form between octane and the urea as well as the clathrate formation of the hexadecane and urea.  
B. Since hexane only has 6 carbon atoms, and the exclusivity of what the urea can accept to create a clathrate, no clathrate can be formed since urea requires the guest compound to be at least 7 carbon atoms and not a branched compound.  
C. The clathrate would decompose considering the melting point of hexadecane is 18 degrees C and in 90 degrees C, the hexadecane would just break from the clathrate formed.  
D. This results in the improper mass acquired which ruins the guest/host ratio to be calculated.

6. Flow Diagram:

