Experiment 5: Colligative Properties *via* Differential Scanning Calorimetry

Procedure

CHE 347 TA: Alec Beaton

Introduction

In this experiment, we will measure the impact of dissolved solutes on the freezing point of a solution. We will deal with solutions of reverse micelles, which are thermodynamically stable nanometer-sized pools of water dispersed in an oil. These solutions consist of water, oil, and surfactant. Depending on the amount of these three components relative to the others, the sample will consist of reverse micelles, as evidenced in the ternary phase diagram below [De and Maitra, 1995]. In this diagram, AOT (Aerosol-OT) is the surfactant, which is one of the most widely studied and readily available surfactants in the literature, and the oil phase is iso-octane.

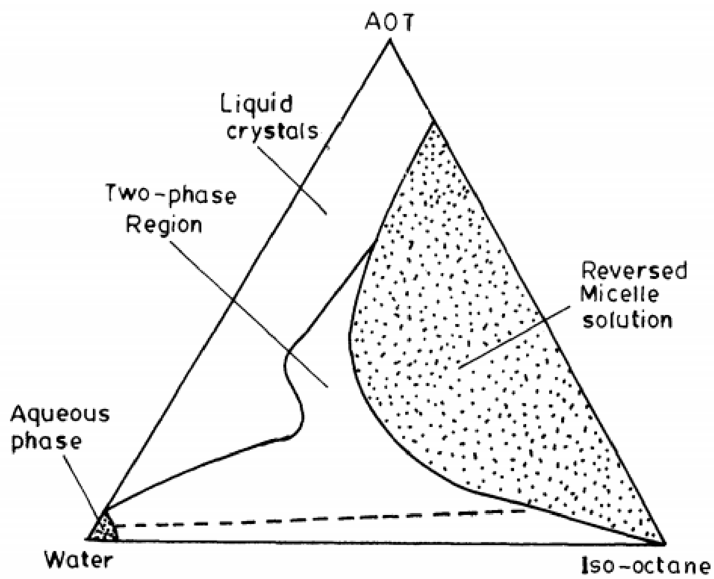


Fig. 2. Phase diagram of water–AOT–isooctane system [22].

In our system, we will use cyclohexane as the oil and AOT as the surfactant. AOT in cyclohexane will aggregate provided that it is above the concentration of AOT is above the critical micelle concentration (CMC) typically considered to be ~1 mM [Smith et al., 2013]. By changing the water loading, $w_0 = \frac{[H_2O]}{[AOT]}$, we can change the size of the reverse micelles. As the reverse micelles increase in size (number of molecules per reverse micelle), the total number of reverse micelles in solution will decrease (and vice versa). We will observe the effect of this phenomenon on the freezing point depression of cyclohexane, whose freezing point in pure solution is 6.50 ℃. The freezing point depression is given by

$$\Delta T = Km \qquad [1]$$

where K is the cryoscopic constant (for cyclohexane, 20.2 K kg mol^{-1}) and m is the osmolality (which is identical to the molality for an ideal solution).

Objectives

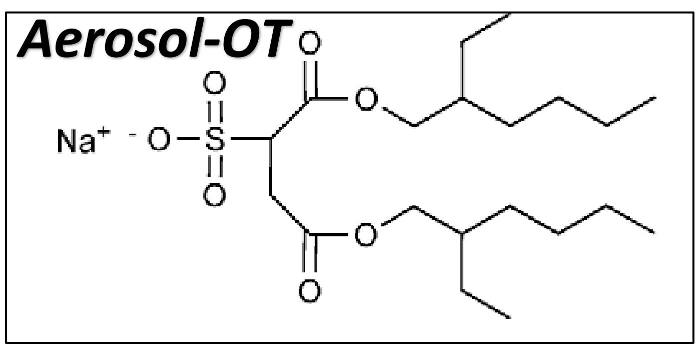
- Prepare and analyze samples for differential scanning calorimetry
- Identify impact of solute aggregation on freezing point depression
- Utilize ternary phase diagram to understand and predict sample properties

Equipment:

- TA Instruments Q2000 Differential Scanning Calorimeter
- Tzero Pans
- Tzero Hermetic Lids
- Tzero Press
- Tzero Die Set
- Drummond Wiretrol I micropipettes (10 µL)

Materials

- Cyclohexane
- Aerosol-OT
- Water



Procedure:

Part I: Sample preparation

You will be provided three reverse micelle solutions as well as a solution of pure cyclohexane. For each of these four solutions, you will need to add 10 µL of solution to a clean pan and crimp the lid using the Tzero press to prepare hermetically sealed samples for the DSC measurement. A capillary micropipette will allow precise control of your sample volume. This procedure will be shown to you by the TA, but you will be responsible for preparing these samples independently.

It is extremely important that the crimped sample pans are clean of *any* residue before inserting into the DSC. When preparing your samples, you should take extra care to work on a clean surface at all times and to only get the sample in the sample pan. Additionally, due to the volatility of cyclohexane, you must measure out the samples and crimp the pans in a timely fashion. We recommend that you have a piece of weigh paper with you so that you never rest the pan on the counter, and (to allow yourself to crimp the pan in a timely fashion) that you plan out the motions needed to add the sample to the pan and crimp it.

Part II: DSC Measurements and analysis

Once the crimped pans are ready, you will insert each one, one at a time, into the DSC. Be sure to always use a reference pan (i.e., crimped pan containing no sample) which will be provided for you. The DSC experiments will take a few minutes to run. When they are complete, you will analyze the data on the computer using the Universal Analysis program provided by TA instruments, and record the temperature at which cyclohexane freezes in each instance.

[1] De, T. K.; Maitra, A. Solution Behaviour of Aerosol OT in Non-Polar Solvents. *Advances in Colloid and Interface Science* **1995**, *59*, 95–193. https://doi.org/10.1016/0001-8686(95)80005-N.

[2] Smith, G. N.; Brown, P.; Rogers, S. E.; Eastoe, J. Evidence for a Critical Micelle Concentration of Surfactants in Hydrocarbon Solvents. *Langmuir* **2013**, *29* (10), 3252–3258. https://doi.org/10.1021/la400117s.

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Post-Lab

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Introductory Information

1. Provide some background information on reverse micelles:
   - What is a reverse micelle?
   - Provide three uses of reverse micelles outside of academic research (you may need to do some research online).

2. What equations will you need to turn the values recorded in your lab notebook into the main values (*i.e.*, meaningful physical quantities) that you wish to report?

3. What does a peak mean in a DSC thermogram?

4. Is freezing an endothermic or exothermic process?

Experimental Details

1. Name the chemicals used in this experiment.

2. Report any additional observations during the course of the experiment.

Results and Discussion

1. Report results in a table for the mass of the crimped sample pans, the freezing points determined for each of the four solutions, along with the corresponding osmolalities (**must include units**)

2. Show the work for calculating the osmolality for one of your samples.

3. Report the water loading for these samples based off of the information provided by the TA on the solution prep.

4. By comparing two of your three datapoints, you should notice a case where you added water to your sample, and the freezing point of the cyclohexane increased. Since the freezing point of cyclohexane should decrease (be depressed) with the increased osmolality of dissolved material, explain this result.

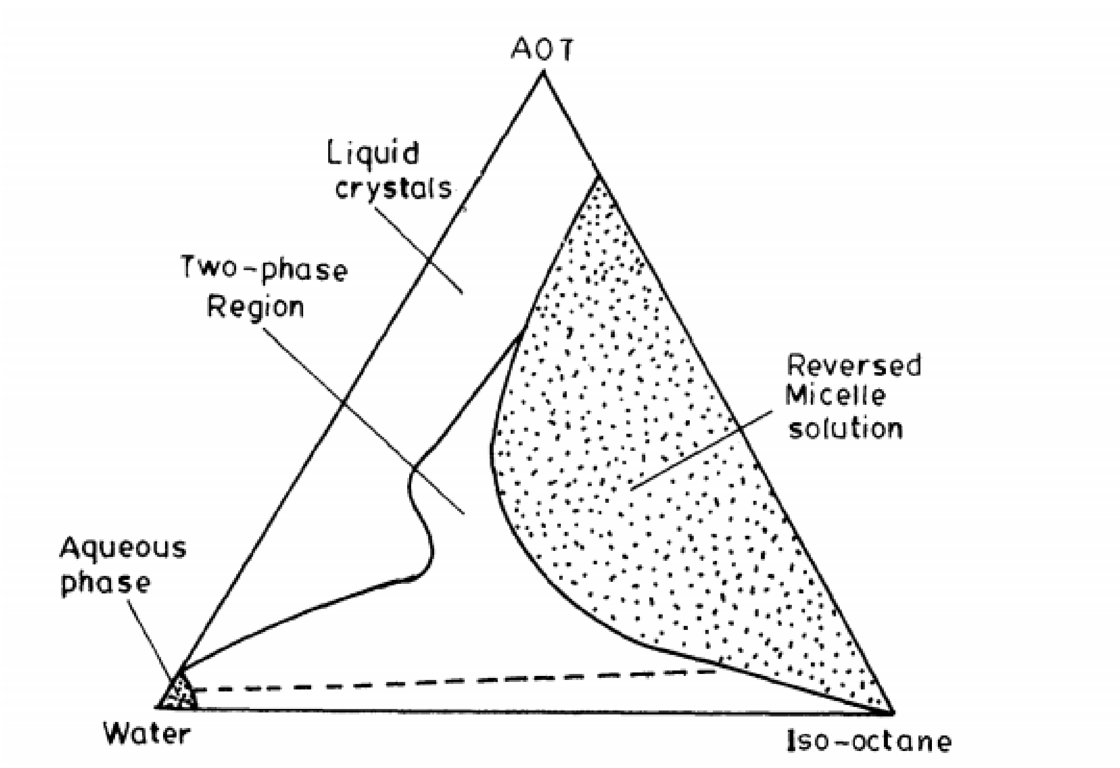
5. Clearly indicate on the ternary phase diagram below where the solutions used in this experiment reside. Show and describe all work used to arrive at this answer.
   Note: Please refer to this link to answer this question (link also provided on Blackboard).

Note: You may assume there is a negligible differences between cyclohexane and iso-octane as the dispersant when it comes to the ternary phase diagram.

6. Would you expect to observe a decrease in the freezing point of cyclohexane in the absence of water in this system? Why or why not?

7. Given a sample contains 600 µL of cyclohexane, 95 µL of water, and 800 mg of AOT, would this sample be considered a reverse micelle solution?

8. Include labeled thermograms as an appendix to your report



Experiment 5: Colligative Properties *via* Differential Scanning Calorimetry (DSC) – Rubric

Student:

Introductory Information (24 pts)

1. (/7 pts)
2. (/7 pts)
3. (/5 pts)
4. (/5 pts)

Total: (/ 24 pts)

Experimental Details (12 pts)

1. (/6 pts)
2. (/6 pts)

Total: (/ 12 pts)

Results (64 pts)

1. (/15 pts)
2. (/5 pts)
3. (/5 pts)
4. (/9 pts)
5. (/9 pts)
6. (/4 pts)
7. (/5 pts)
8. (/12 pts)

Total: (/ 64 pts)

Report Total: (/ 100 pts)

General Comments: