Chemistry 213

CALCULATING THE ACTIVATION ENERGY OF A DEMUSIFICATION PROCESS

LEARNING OBJECTIVES

After completing this experiment, students will be able to:

- summarize the processes of emulsion and demulsification at a molecular level.

- articulate the relationship between temperature and the rate of a chemical or physical process.

- calculate the activation energy of a process using the Arrhenius equation.

BACKGROUND

Emulsions

Emulsions form when immiscible liquids are mixed and small droplets of one liquid become dispersed in the other. Emulsions populate the food industry with such products as milk, cream liqueurs and sauces such as Italian salad dressings. Lotions, makeup and nail polish are examples of emulsions found in the cosmetic industry. In the late 1800s and early 1900s, wildcatters (prospectors who searched for oil-rich ground) extracted oil from the earth by pumping water down the well, thus forming an emulsion. Due to the added water pressure the oil/water emulsion would rise to the surface and the demulsification process occurred afterward.

Emulsions form when two or more liquids of differing polarities are combined. Liquids with different polarities will experience different combinations of intermolecular forces. Take oil and water as an example: these have significantly different polarities. Oil is highly nonpolar whereas water is quite polar. As a result, oil molecules experience only London dispersion forces, which are relatively weak, whereas water molecules experience London dispersion forces plus dipole-dipole and even hydrogen bonding forces. The water molecules will be held together relatively tightly due to these stronger intermolecular forces, and oil molecules will not easily be able to insert themselves among the water molecules. Because of this, oil and water will not combine into a single-phase mixture. They will separate into two phases based on their intermolecular forces and densities. When mixed, the denser liquid settles to the bottom and the less dense liquid rises to the top. Upon agitation of the emulsion the two phases will briefly mix, resulting

in a single phase. Droplets of the nonpolar phase (held together by weaker forces) will disperse themselves amidst the polar phase (held together by stronger forces). When left undisturbed, emulsions eventually demulsify once again and form two phases with the denser substance resting at the bottom and the less dense component rising to the top.

The processes of emulsion and demulsification are physical (not chemical) processes. Even so, we can imagine an energy diagram for the demulsification process as shown in Figure 1. The emulsion is less stable (higher in energy) than the separated phases. In order for the system to move from an emulsion to separated liquid phases, various droplets of one phase (e.g. the nonpolar phase) must move through the other phase (e.g. the polar phase) and coalesce into larger droplets. This requires an even higher energy than the emulsion itself. In other words, the system must overcome an activation energy barrier in order to demulsify. In this lab, the specific system of interest is an emulsion of isopropanol in a saltwater solution, NaCl(*aq*). The rate at which this system demulsifies at different temperatures is used to calculate the value of the activation energy (E_a) of the demulsification process.
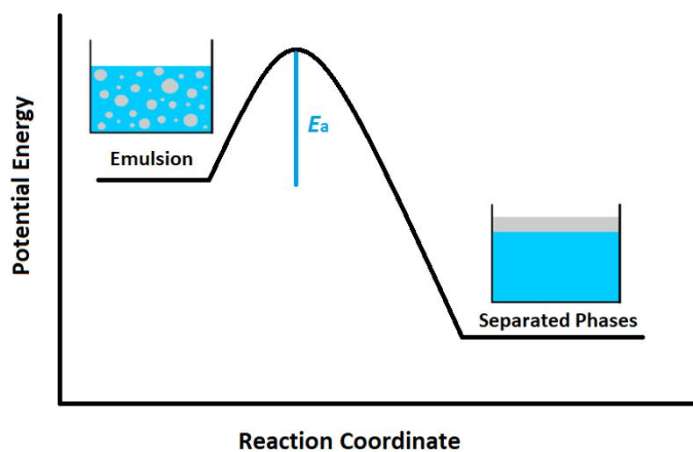

Figure 1. Reaction energy diagram for demulsification .

Theoretical Background:
The Arrhenius equation relates the rate constant of a process to the temperature at which the process is carried out and the activation energy of that process. The Arrhenius equation states that the rate constant, k, equals the frequency factor, A (a constant), multiplied by the exponential value of the negative of the energy of activation , E_a, divided by the ideal gas constant, R, and the absolute temperature, T:

$$k = Ae^{\frac{-E_a}{RT}} \qquad (1)$$

Taking the natural logarithm of equation (1) results in the following

$$\ln k = -\frac{E_a}{RT} + \ln A \qquad (2a)$$

Or, put another way,

$$\ln k = \left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \qquad (2b)$$

In order to use the Arrhenius equation to find the activation energy, the unknown value of the rate constant (k) must be determined or else somehow replaced by known quantities. To do this, we use the fact that the rate of the demulsification process in the mixture of isopropanol and NaCl(*aq*) can be represented as

$$\text{rate} = k[\text{idrops}]^n \qquad (3)$$

where k is the rate constant of the process, [idrops] is the concentration of the isopropanol droplets suspended in the polar aqueous phase, and n is the order of the reaction.

There is evidence to suggest that in this experiment the process of demulsification is a zero-order process; in other words, for this experiment, it is likely that $n = 0$. Therefore, equation 3 becomes

$$\text{rate} = k[\text{idrops}]^0 \qquad (4a)$$

or, in other words,

$$\text{rate} = k \quad [\text{for this particular experiment}] \qquad (4b)$$

Because in this case rate $= k$, we can rewrite equation 2b using the reaction rate (which we can directly measure) instead of the rate constant (which is not directly measured):

$$\ln(\text{rate}) = \left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \qquad (5)$$

Equation 5 shows that plotting $\ln(\text{rate})$ against the inverse of the temperature, $1/T$, will yield a straight line with a slope of $-\frac{E_a}{R}$ and a y-intercept of $\ln A$. The slope of this plot can be used to determine the activation energy of the demulsification process, E_a.

SAFETY PRECAUTIONS AND WASTE DISPOSAL

Isopropanol may cause skin and eye irritation. Any skin contact with isopropanol should be immediately washed. Safety goggles must be worn in the lab at all times. Wash hands with soap and water before leaving the lab. If possible, salvage and rinse the beads for later use. Dispose of the alcohol and saltwater according to the directions of your instructor or teaching assistant.

EXPERIMENTAL PROCEDURE

Supplies Needed
- two 200-mL beakers
- two 10-mL graduated cylinders
- one 50- or 100-mL graduated cylinder
- balance (with at least 0.01 g precision)
- hot plate
- one 2-L soda bottle preform with cap
- timer/stopwatch (with at least 0.1 second precision)
- thermometer or digital thermistor (with at least 0.1°C precision)
- LDPE beads (about 5)
- 99% isopropanol (10 mL)
- NaCl(s) (about 2.2 g)
- DI or distilled water (at least 10 mL, plus about 5 mL more for rinsing)
- ring stand and clamp (optional)

- 250 mL Erlenmeyer flask (optional; works well as a "stand" for the preform)

Measurements

1. Set up the following for later use:

   a. a 200-mL (or larger) beaker filled ¾ full with ice water.

   b. A 200-mL (or larger) glass beaker filled ¾ full with water. Place this on a hot plate. (Wait to turn on the hot plate.)

2. Obtain a soda bottle preform and cap. Remove the plastic ring from the bottom of the cap. Use isopropyl alcohol followed by water to rinse out the soda bottle preform to make sure that no residue will contaminate the emulsion.

3. Measure and record the masses of two clean, dry 10-mL graduated cylinders. (Be sure to keep straight which mass corresponds to which graduated cylinder. One will be used to hold salt water, the other will be used to hold isopropanol.)

4. Measure out 2.2g NaCl(*s*) onto a weigh boat or weigh paper and transfer it into the preform.

5. With a 100-mL graduated cylinder, add 10 mL of DI water to the salt, making sure the salt dissolves completely by shaking it.

6. Upon the combination of the NaCl and H_2O the volume of the solution will be greater than 10 mL; therefore, the excess must be removed. Measure 10.0 mL of your saltwater solution in one of your clean, dry 10-mL graduated cylinders. Discard any excess salt water from the preform, and pipet out any excess salt water from the graduated cylinder. (The excess salt water can be tossed down the drain; it is good practice to run water while you do this.)

7. Record the mass of the 10.0 mL of salt water in the 10-mL graduated cylinder. Use this information to find the density of the saltwater solution.

8. Return the 10mL of the saltwater solution back into the preform. Clean and dry the graduated cylinder for later use.

9. Using a different clean, dry graduated cylinder, measure out 10.0 mL of isopropanol and record its mass (in order determine its density later). After the mass has been recorded, add the isopropanol to the preform containing salt water. Clean and dry the graduated cylinder for later use.

10. To set the solution, it must be agitated and then left to separate a minimum of 3 times. Agitate the solution by gently inverting it several times to form an emulsion (shaking the solution too vigorously can yield an overly stable emulsion that does not demulsify quickly). Once the solution is set, add 5 beads. The beads will be used to more easily observe the demulsification of the emulsion. (Upon agitating or shaking the emulsion the beads will rise to the top of the solution; as the emulsion separates the beads will settle down and rest on the interface on top of the salt water and alcohol interface.)

11. Measure the initial temperature of the solution using a digital thermometer. When using the thermometer, unscrew the cap of the preform and swirl the solution around the thermometer to get an accurate measure of the temperature.

12. Record the temperature, then agitate the emulsion by inverting it several times and quickly set the preform in a 250-mL Erlenmeyer flask so that it remains steady and upright during the demulsification process. As soon as the preform is set in the flask, start a timer and measure how long it takes for the emulsion to separate. Stop the timer once the beads are settled and the bubbling at the interface stops. Repeat this three times at the same temperature, recording the time of each demulsification.

    - *NOTE:* you do not need to take the temperature of the mixture for each of the three trials and/or try to restore the temperature of the mixture to exactly the same value each time. Simply take the temperature right before the first trial and then perform the remaining trials. You may assume that the temperature of the mixture remains at the same value as the first trial. This is an approximation, but it works well as long as it doesn't take more than 3-4 minutes to complete all three trials. If you are interrupted and unable to complete all three trials within 3-4 minutes, then you will need to try to restore the temperature of the solution to the original value.

    - *IMPORTANT*: be consistent in the number of times that you invert the solution to form the emulsion for each trial. About 5-10 inversions of the preform should be plenty.

13. Place the preform in the ice bath and measure the temperature of the solution in the preform. You will need to *continually stir the solution* with the thermometer in order to get an accurate temperature reading. Keep the preform in the ice bath until its temperature has fallen to 5°C below the initial temperature. Place the cap back on the preform and repeat step 12 at this temperature. *Note:* When cooling the solution, make sure to watch it carefully. If you allow it to get too cold the salt will precipitate out of the solution. Sometimes the solution may need to be reheated before timing the demulsification.

14. Clamp or hold the preform so that it is suspended in the beaker on the hot plate (the water level in the beaker should be higher than the level of liquid in the preform). Gently heat the water in the hot plate until the temperature of the solution in the preform is 5°C above the initial temperature. (Again, you will need to continually stir the solution to get an accurate temperature reading.) Repeat step 12 at this temperature.

15. Repeat step 14 for temperatures that are 10°C and 15°C above the initial temperature.

16. Using the clean (and hopefully now dry) pre-weighed 10-mL graduated cylinders, find the density of each liquid phase after they have separated.

    a. Find the mass of the empty graduated cylinders.

    b. Carefully pipet the supernatant (that is, the top liquid phase) into a pre-weighed 10-mL graduated cylinder (called graduated cylinder #2 on data sheet). Record its volume and mass. Use that data to calculate the density of the supernatant.

c. Carefully pipet the lower liquid phase into another pre-weighed 10-mL graduated cylinder (called graduated cylinder #1 on data sheet). Record its volume and mass. Use that data to calculate the density of the lower liquid phase.

Data Analysis

1. Once you have gathered times for five different temperatures (three trials each), average the times for each temperature.

2. Find the densities of the salt water solution and isopropyl alcohol. First decant off the supernatant and determine its density. Next, determine the density of the bottom layer.

3. Set up a table in Excel similar to the one below:

Temp (°C)	Temp (K)	Time (s)	$1/T$ (K^{-1})	rate (s^{-1})	ln(rate)

a. In the "Temp (°C)" column, fill in the five temperatures at which you performed demulsifications in degrees Celsius (same as those recorded on your data table).

b. In the "Temp (K)" column, convert each of the five temperatures into Kelvin.

c. In the "Time (s)" column, record the average time (over three trials) that was required to demulsify the emulsion at each of the five temperatures.

d. In the "$1/T$ (K^{-1})" column, find one divided by the given temperature in Kelvins.

e. In the "rate (s^{-1})" column, find one divided by the average time of demulsification at the given temperature. (This is because a reaction rate is always an amount of substance per unit time. In this lab we are always using the same amount of mixture, so we just call that amount one "unit" of mixture. Here we are calculating the rate of "units" of mixture per second that demulsifies.)

f. In the "ln(rate)" column, find the natural logarithm of the rate (given in the previous column) at each of the five temperatures.

IMPORTANT: After creating and completing the data table above in Excel, be sure to copy and paste your data table into the shared Google spreadsheet for this class. The instructor will provide you with the appropriate link.

4. After completing table above, use Excel to create a plot of ln(rate) vs. $1/T$. That is, ln(rate) should be on the y-axis and $1/T$ should be on the x-axis. Be sure to give your graph a title, label the axes correctly, and scale the axes so that the graph is easy to read.

5. Use Excel to plot a line of best fit (that is, a linear trendline) through the data points on your plot of ln(rate) vs. $1/T$. Be sure to include the equation of the line and the R^2 value on your plot. Print out this plot and include it with your report.

6. As shown in Equation 5 above, the slope of the line of best fit through a plot of ln(rate) vs. $1/T$ will be equal to $-E_a/R$. Use this relationship to find the activation energy (E_a) of the demulsification process. (As always, be sure to show your work clearly, including units.)

CALCULATING THE ACTIVATION ENERGY OF A DEMUSIFICATION PROCESS
Data Sheet (Experimental Data)

Densities of NaCl(aq) and Isopropanol Before Emulsion

Mass of clean, dry 10-mL graduated cylinder #1 (for salt water): _____

Mass of clean, dry 10-mL graduated cylinder #2 (for isopropanol): _____

Mass of graduated cylinder #1 + NaCl(aq): _____

Mass of graduated cylinder #2 + isopropanol: _____

Mass of 10.0 mL of NaCl(aq): _____

Mass of 10.0 mL of isopropanol: _____

Density of NaCl(aq): _____

Density of isopropanol: _____

Densities of Isopropanol and Aqueous Phase After Emulsion and Demulsification

Mass of clean, dry 10-mL graduated cylinder #1 (for aq phase): _____

Mass of clean, dry 10-mL graduated cylinder #2 (for isopropnanol): _____

Mass of graduated cylinder #1 + lower phase (aq phase): _____

Mass of graduated cylinder #2 + supernatant (isopropanol): _____

Mass of lower phase (aq phase): _____

Mass of supernatant (isopropanol): _____

Volume of liquid in graduated cylinder #1 (aq phase): _____

Volume of liquid in graduated cylinder #2 (isopropanol): _____

Density of aqueous phase: _____

Density of supernatant: _____

Kinetics of Demulsification

Original Data:

Temperature	Time required (s) for emulsion to separate (demulsify)			
	Trial 1	**Trial 2**	**Trial 3**	**Average**
T_1=Initial T(K) =				
T_2= T_1(K)-5K =				
T_3=T_1(K)+5K =				
T_4=T_1(K)+10K =				
T_5=T_1(K)+15K =				

Data Analysis:

Average Temp (°C)	Average Temp (K)	Time (s)	$1/T$ (K^{-1})	rate (s^{-1})	ln(rate)

Slope of plot of ln(rate) vs $1/T$ (include units): _____

Activation energy (E_a) of demulsification process (include units):_____