

Vapor-Liquid Equilibrium of Hydrocarbon Mixtures

Goal: To determine whether hydrocarbon mixtures obey Raoult's law.

Background: In the first experiment you measured the mutual solubility of butanol and water. The fact that the mixtures were only partially miscible was a consequence of the disparity in bonding energies between the components of the mixture and those of the pure components. Some of you noted that, after mixing, the top layer was at a different temperature than the bottom. This is a direct consequence of the mismatch in bonding between the components. Had the bonding interactions been the same, the temperature would not have changed. This is referred to as athermal mixing. It is one of the signatures of **ideal solutions**. However, it isn't the only criterion that must be met. In addition to realizing no change in bonding upon mixing, components comprising an ideal solution also must exhibit a comparable entropy change upon being mixed. This later criterion depends on molecular size, and is therefore harder to meet.

In the general case, the entropy change upon mixing is difficult to measure directly. However, the properties of the components in the liquid are reflected in the behavior of the gas mixture that is in equilibrium with it. Therefore, ideal solutions are defined in terms of this vapor-liquid equilibrium. A practical statement of ideal solution behavior is **Raoult's law**. The ideal solution follows Raoult's law for all components in the mixture. Put in mathematical form, Raoult's law is given by:

$$y_i P = x_i P_i^{sat} \quad (1)$$

where x_i and y_i are the mole fractions of component i in the liquid and gas phases, respectively. P is the system pressure, and P_i^{sat} is the saturation pressure of component i at the temperature of the mixture. Because of the obvious importance of hydrocarbons in oil refining and as raw materials for synthetic chemicals, their saturation pressures are well known. Their values are usually given as coefficients to the **Antoine equation**.

$$\log_{10} P_i^{sat} = A - \frac{B}{T + C} \quad P_i^{sat} \text{ in mmHg} \quad (2)$$

Here T is the Kelvin temperature. Values for A , B , and C for several hydrocarbons are given in the Table 1.

Table 1: Antoine Parameters for Several Hydrocarbons.

Substance	A	B	C
n-hexane	6.87601	1171.17	-48.74
cyclohexane	6.84498	1203.53	-50.29
n-octane	6.91868	1351.99	-64

If Raoult's law defines ideal solution behavior, then a deviation from Raoult's law should give a measure of the non-ideality of the solution. To describe the extent of non-ideality chemists use a parameter called the activity coefficient, γ_i . The subscript i

indicates that each component may in fact have a different activity coefficient. We define the activity coefficient with respect to the Raoult's law reference state.

$$\gamma_i = \frac{y_{i,actual}}{y_{i,Raoult's}} \quad (3)$$

For sufficiently low pressures, the vapor phase will behave like an ideal gas. In this case, the partial pressure of component i above the liquid solution is given by:

$$y_i P = \gamma_i x_i P_i^{sat} \quad (4)$$

The only difference between expression (4) and Raoult's law is the activity coefficient. Therefore, an activity coefficient of one indicates that the liquid is behaving like an ideal solution. Activity coefficients greater than one give rise to elevated vapor pressures. The dissimilar components essentially try to avoid each other, escaping to the vapor phase. Likewise, activity coefficients less than one indicate a net attraction between dissimilar components. In general, activity coefficients may be greater than one for some components and less than one for others. For a binary mixture; however, the activity coefficients represent the same interaction. Consequently, the values of γ_1 and γ_2 are related. The simplest relationship is given by:

$$\ln \gamma_1 = K x_2^2 \quad \ln \gamma_2 = K x_1^2 \quad (5)$$

Note, in the limit that x_2 approaches 0 (pure component 1) the activity coefficient for component 1 asymptotically approaches unity. Here most molecules of type one are surrounded by like molecules. Therefore, this component should behave as if in an ideal solution. The activity coefficient for component 2; however, approaches e^K . This represents the interactions of molecule 2 surrounded by all component 1 molecules.

The gas phase mole fraction can be measured in various ways. In this experiment you will use the technique of head space chromatography to determine the gas phase concentration. The mixtures you will consider are n-hexane/n-octane and n-hexane/cyclohexane. Since these are all small hydrocarbons, we would expect athermal mixing in these mixtures. However, since the components are of different sizes, we would expect non-ideal solution behavior. This allows us to formulate the hypothesis for the experiment.

Hypothesis: Both n-hexane/n-octane and n-hexane/cyclohexane will exhibit non-ideal solution behavior as evidenced by activity coefficients that are different than 1. The deviations from ideality of the n-hexane/n-octane solution will be greater since the size disparity of the components is greater.

Experimental:

Reagents:

- n-hexane
- n-octane
- cyclohexane
- helium (if necessary)

Main Apparatus:

Gas Chromatograph/Mass Spectrometer
12 Conical Head Space Vials with PTFE Septum Tops
10 μL GC Syringe
100 μL Gastight GC Syringe
Digital Balance
3, 5 mL Graduated Pipets
Pipet Bulb

Procedure:

First Day

- 1) Prepare a mixture containing 0.5 mL each of n-hexane, n-octane and cyclohexane in one of the head space vials, placing a cap on the mixture after it has been prepared.
- 2) Familiarize yourself with the software for the GC/MS.
- 3) Set up a run, using column B, starting at 40 °C for an initial period of 3 minutes, then ramping to 200 °C at 20 °C/min.
- 4) Inject 0.5 μL of the liquid mixture and record a chromatograph.
- 5) Refine the procedure in step 3 to enable you to remove the air peak (set solvent delay, or define mass range), and get a good separation of the three main components.
- 6) Using the conditions established in step (5), record two more chromatographs for the liquid hydrocarbon mixture.
- 7) Set up the instrument to record the chromatograph of the head-space vapor. I recommend decreasing the split ratio to 2.
- 8) Using the 100 μL Gastight GC syringe draw up 20 μL of the head-space vapor of hydrocarbon mixture. In one fluid motion inject the gas into the GC and start the run.
- 9) Repeat step 8 for 4 more trials. These runs will be used to give an estimate for the precision of the technique.
- 10) The peak areas need to be converted to mole fractions. Using the liquid data, set up the proportions:

$$C_{oct} = \frac{A_{oct} x_{hex}}{A_{hex} x_{oct}} \quad C_{cyc} = \frac{A_{cyc} x_{hex}}{A_{hex} x_{cyc}}$$

Here, A_{oct} and x_{oct} represent the peak area and mole fraction for octane, respectively.

Second Day

- 1) Using clean head space vials, prepare mixtures of n-octane in n-hexane having 15, 30, 45, 60, 75 and 90 mole % octane, respectively. Place septum tops on the vials and allow them to come to thermal equilibrium. (~10 minutes).
- 2) Record the temperature in the lab.

- 3) Starting with the vial containing the least octane, record chromatographs of the head space vapors of the mixtures using the method file that you developed the prior week.
- 4) Integrate the peaks of the chromatographs.
- 5) Using the proportionality factor, C_{oct} , determine the mole fraction for octane in the vapor phase, y_{oct} . The relationship is:

$$y_{oct} = \frac{A_{oct}/A_{hex}}{C_{oct} + A_{oct}/A_{hex}}$$

- 6) Make a graph of mole fraction of n-octane in the vapor versus mole fraction of n-octane in the liquid.
- 7) Determine the saturation pressure for n-hexane and n-octane using the Antoine equation. On the graph created in step 6 plot the x-y relationship predicted by Raoult's Law for the n-hexane/n-octane system.
- 8) Use equation 4 to develop a relationship for the ratio of the activity coefficients, $\gamma_{oct}/\gamma_{hex}$. If we combine the relationships in expression (5) we can get a relationship for the parameter K:

$$\ln\left(\frac{\gamma_{oct}}{\gamma_{hex}}\right) = K(x_{hex}^2 - x_{oct}^2)$$

Make a graph of this relationship to determine the value of K. A value of K=0 indicates ideal solution behavior.

- 9) Determine the confidence limit for K. Is it different than zero?

Third Day

- 1) Repeat the study from day 2, interchanging cyclohexane for n-octane.
- 2) Discuss whether the hypothesis is valid or if it can be refuted based on your experimental data.