

Miscibility of Mixtures of Cyclohexane and Methanol

Purpose

Miscibility of binary liquid mixtures of methanol and cyclohexane will be studied. A two-phase distribution ratio will be determined. Temperature and composition of the liquid-liquid critical point will be determined.

Introduction

The mutual solubility or miscibility of two liquids is a function of temperature and composition. When two liquids (A and B) are partially soluble in each other, two liquid phases can be observed.¹⁻³ At equilibrium, each phase contains A and B in amounts that reflect their mutual solubility. Some systems are totally miscible (i.e. they form a one-phase liquid) at high temperatures, but separate into two liquid phases at lower temperatures. These systems have an upper consolute temperature, T_C , in a plot of temperature versus mole fraction. Other systems are totally miscible at low temperatures but separate into two phases at higher temperatures giving rise to a *lower* consolute temperature, T_C .

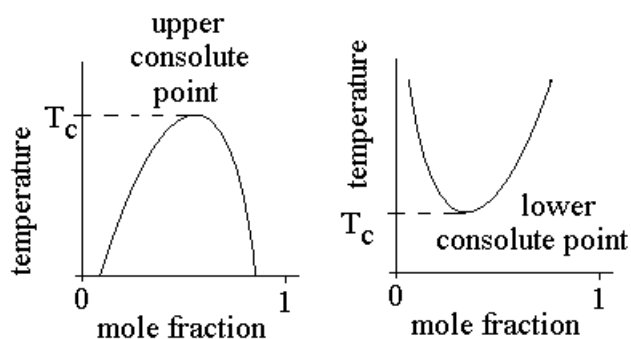


Figure 1

The binary liquid system studied in this lab is the methanol-cyclohexane system.^{1,4-7} The distribution ratio will be measured for the methanol-cyclohexane system.

$$K_A = d_{AU}/d_{AL} \quad \text{or} \quad d_{AL}/d_{AU} \quad (1)$$

Where “U” and “L” refer to “upper” and “lower” liquid phases, and “A” stands for methanol. The direction of the ratio, upper over lower or *vice versa*, is immaterial. The usual convention is to make K_A greater than unity. After collecting data for K_A , several mixtures of methanol and cyclohexane will be prepared in order to construct a phase diagram of temperature *versus* mole fraction cyclohexane. The initial temperature for each solution is selected so that only one phase is observed. Then the temperature is slowly lowered until two liquid phases are observed. This is the temperature for the phase transition and this temperature depends on the composition or mole fraction of the solution.

The transition between the one-phase and two-phase regions is represented by the curved lines in Figure 1. When the solution (one phase) of a fixed mole fraction composition passes through this curve (to two phases) as the temperature is varied, the solution strongly scatters light. In this

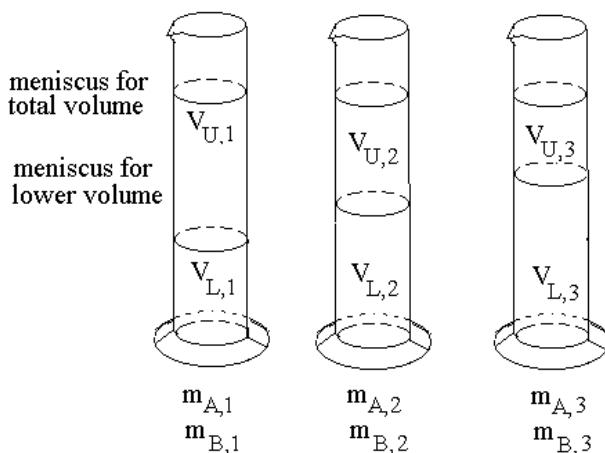
experiment, a binary solution of known composition is prepared at a temperature at which it is totally miscible. A laser beam is passed through this one-phase solution and the beam that emerges from it is observed as a function of temperature. When the system approaches the transition temperature, the laser beam is scattered. The temperature of maximum scattering is recorded as a single point on the curved transition line. Solutions of other mole fraction compositions are similarly studied to construct the entire phase diagram. This method does not require the removal of sample from the system.

Experimental Plan

I. Determining the Distribution Ratio at 25°C

The distribution ratio of component A is a thermodynamic quantity that describes the equilibrium ratio of the amount of A in the two liquid phases that form when A and B are mixed at constant temperature. In order to determine this K_A value, three samples are prepared, with an approximate volume ratio of A:B = 1:3 (Sample I), A:B = 1:1 (Sample II) and A:B = 1.5:1 (Sample III). Two phases form when A and B are mixed. From the volumes of the two phases and the masses of A and B, one can calculate the densities of A and B in the two phases.

Use 10-mL graduated cylinders that have ground-glass stoppers. Measurements should be carried out using a water bath to maintain the temperature at 25°C.



The masses and volumes in any particular sample are related by the densities. In sample i ($i=1, 2, \text{ or } 3$):

$$m_{A,i} = d_{A,U} V_{U,i} + d_{A,L} V_{L,i} \quad (2)$$

$$m_{B,i} = d_{B,U} V_{U,i} + d_{B,L} V_{L,i} \quad (3)$$

The A and B equations can conveniently be combined into a single matrix equation:

$$\begin{pmatrix} m_{A,i} \\ m_{B,i} \end{pmatrix} = \begin{pmatrix} d_{A,U} & d_{A,L} \\ d_{B,U} & d_{B,L} \end{pmatrix} \begin{pmatrix} V_{U,i} \\ V_{L,i} \end{pmatrix} \quad (4)$$

or more simply,

$$m_i = \underline{\underline{d}} V_i \quad (5)$$

Because all three samples are held at the same temperature, the $\underline{\underline{d}}$ matrix is the same for all samples. The m_i and V_i vectors differ among the three samples. We need to calculate the densities from the experimentally measured masses and volumes. There are more mass and volume data than there are unknown parameters (densities) so our problem is (blessedly) overdetermined. Two methods for calculating the densities are (a) linear least squares; and, (b) pairwise combination of sample data. Use the method you prefer or use both. After you calculate densities, calculate K_A and K_B .

(method a) linear least squares

Define the total square error

$$\varepsilon^2 = \sum_{i=1}^3 (m_i - \underline{\underline{d}} V_i) \bullet (m_i - \underline{\underline{d}} V_i) \quad (6)$$

Minimizing ε^2 with respect to the elements of $\underline{\underline{d}}$ leads to the matrix equation

$$\underline{\underline{X}} = \underline{\underline{d}} \underline{\underline{Y}} \quad (7)$$

where

$$\begin{aligned} X_{1,1} &= \sum_{i=1}^3 m_{A,i} V_{U,i} & Y_{1,1} &= \sum_{i=1}^3 V_{U,i}^2 \\ X_{1,2} &= \sum_{i=1}^3 m_{A,i} V_{L,i} & Y_{1,2} &= Y_{2,1} = \sum_{i=1}^3 V_{U,i} V_{L,i} \\ X_{2,1} &= \sum_{i=1}^3 m_{B,i} V_{U,i} & & \\ X_{2,2} &= \sum_{i=1}^3 m_{B,i} V_{L,i} & Y_{2,2} &= \sum_{i=1}^3 V_{L,i}^2 \end{aligned} \quad (8)$$

Calculate the elements of the $\underline{\underline{X}}$ and $\underline{\underline{Y}}$ matrices. Then invert $\underline{\underline{Y}}$ and calculate $\underline{\underline{d}}$.

$$\underline{\underline{d}} = \underline{\underline{X}} \underline{\underline{Y}}^{-1} \quad (9)$$

where $\underline{\underline{Y}}^{-1}$ is, of course, the inverse matrix of $\underline{\underline{Y}}$. Individual densities are the elements of the $\underline{\underline{d}}$ matrix, as shown in equation 4. Recall that calculating the inverse of a 2X2 matrix is simple.

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix}^{-1} = \frac{1}{ad - bc} \begin{pmatrix} d & -b \\ -c & a \end{pmatrix} \quad (10)$$

(method b) pairwise combination of sample data

Any two samples (1 and 2, 1 and 3, or 2 and 3) suffice to calculate all four densities. Choose two samples, 1 and 2, for example. Make mass and volume matrices in which the columns are m_1 , m_2 , V_1 and V_2 (all four are vectors).

$$\begin{pmatrix} m_{A,1} & m_{A,2} \\ m_{B,1} & m_{B,2} \end{pmatrix} = \begin{pmatrix} d_{A,U} & d_{A,L} \\ d_{B,U} & d_{B,L} \end{pmatrix} \begin{pmatrix} V_{U,1} & V_{U,2} \\ V_{L,1} & V_{L,2} \end{pmatrix} \quad (11)$$

Invert the volume matrix (recall equation 10) and calculate the densities.

$$\begin{pmatrix} d_{A,U} & d_{A,L} \\ d_{B,U} & d_{B,L} \end{pmatrix} = \begin{pmatrix} m_{A,1} & m_{A,2} \\ m_{B,1} & m_{B,2} \end{pmatrix} \begin{pmatrix} V_{U,1} & V_{U,2} \\ V_{L,1} & V_{L,2} \end{pmatrix}^{-1} \quad (12)$$

Repeat the density calculation with the other two combinations (1,3 and 2,3). You will then have three values for each of the densities. Calculate their means and uncertainties (e.g., standard deviations). Use the means in all further calculations. Unfortunately, no literature values are known for comparison.

Either method method a or method b leads to four densities: $d_{m,U}$, $d_{c,U}$, $d_{m,L}$ and $d_{c,L}$, where $d_{m,U}$ stands for the density of methanol in the upper layer, $d_{c,U}$ stands for the density of cyclohexane in the upper layer, and so on. Use these four densities to calculate the mole fractions cyclohexane in the two phases that coexist at 25°C, as follows. Consider first the upper layer. In a 100-mL layer, the moles of methanol and cyclohexane would be

$$n_{m,U} = d_{m,U} \times 100\text{mL} / (32.0 \text{ g/mol}) \quad \text{and} \quad n_{c,U} = d_{c,U} \times 100\text{mL} / (84.2 \text{ g/mol}) \quad (13)$$

The mole fraction cyclohexane in that layer would be

$$x_{c,U} = n_{c,U} / (n_{m,U} + n_{c,U}) \quad (14)$$

Calculate $x_{c,U}$ and likewise $x_{c,L}$. Those two mole fractions give two additional points for the graph that will be constructed in part II.

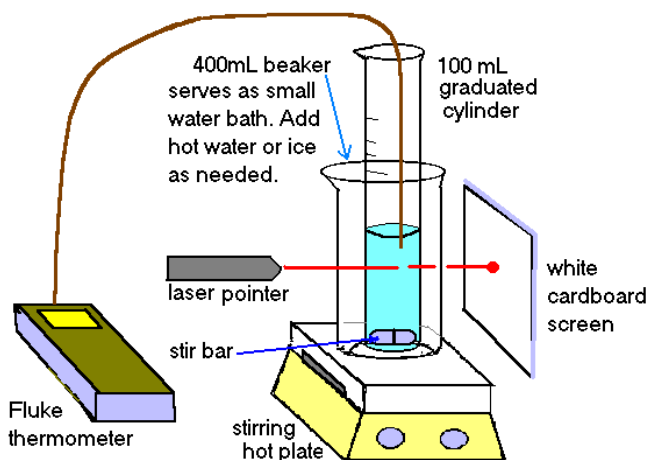
II. Determine the Critical Point of the Methanol-Cyclohexane System

Several solutions of methanol and cyclohexane will be prepared in order to construct a phase diagram of temperature *versus* mole fraction cyclohexane. The initial temperature for each solution is selected so that only one phase is observed. Then the temperature is slowly changed (lowered in this case) until two liquid phases are observed. This is the temperature for the phase transition and this temperature depends on the composition or mole fraction of the solution.

The transition between the one-phase and two-phase regions is represented by the curved lines in Figure 1. When the solution (one phase) of a fixed mole fraction composition passes through this curve (to two phases) as the temperature is varied, the solution strongly scatters light. In this experiment, a binary solution of known composition is prepared at a temperature at which it is totally miscible. A laser beam is passed through this one-phase solution and the beam that emerges from it is observed as a function of temperature. When the system approaches the transition point, the laser beam is scattered. The temperature of maximum scattering is recorded as a single point on the curved transition line. Solutions of other mole fraction compositions are similarly studied to construct the entire phase diagram. This method does not require the removal of sample from the system.

Equipment for binary liquid-liquid phase coexistence curves

- He-Ne laser
- Thermocouple and temperature display
- stirring hot plate and stir bar
- Ice for ice bath
- 100 mL graduated cylinder
- 400 mL beaker



Complete these tables before coming to lab.

	methanol	cyclohexane
Density (g/mL)		
Molecular Mass (g/mol)		

Cyclohexane			Methanol			
ml	mol	mole fraction	add ml	total ml MeOH	mole	mole fraction
24			1	1		
24	“ “		1	2		
24	“ “		2	4		
24	“ “		2	6		
24	“ “		2	8		
24	“ “		6	14		
24	“ “		10	24		
24	“ “		10	34		
24	“ “		15	49		

Experimental Procedure

Determine the distribution coefficient of the methanol-cyclohexane system.

1. Tare a capped 10 mL graduated cylinder. Use a disposable pipet to add about 2 mL methanol. Record the mass (m_A) and initial volume of methanol. Then add about 6 mL cyclohexane to produce a volume ratio of methanol:cyclohexane (A:B) = 1:3. Record the total mass and then determine mass (m_B) and the approximate initial volume of cyclohexane. This is Sample 1.
2. Prepare Samples II and III and label each graduated cylinder. Make sure you record $m_{A,1}$, $m_{B,1}$, $m_{A,2}$, $m_{B,2}$, $m_{A,3}$ and $m_{B,3}$ and the initial volume of each component in each sample.
3. Invert the graduated cylinders several times to mix, occasionally venting the solutions. Place the graduated cylinders in the 25°C water bath. While thermal equilibrium is being approached, continue to invert the graduated cylinders and vent the solutions. Allow about one minute between mixings. Note the formation of the meniscus between the two phases. If the phases do not separate cleanly (e.g. Sample 3), gently tap the graduated cylinder on a firm surface such as a notebook. Allow about 15 minutes for equilibrium to be achieved.

II. Construct the temperature-composition phase diagram for the methanol-cyclohexane system

Use the volumes listed in the pre-lab calculations.

1. Make the first solution of the two components in a 100 mL graduated cylinder. Run the stirrer fast enough to mix but not fast enough to create a deep vortex or bubbles.
2. If the solution separates into two phases, heat it until the phase boundary disappears. However, heat to no more than 55 °C because temperatures above 55°C cause rapid evaporation of methanol.
3. Use cool water and ice as necessary in the beaker water bath to cool the solution while observing the laser beam and the temperature of the solution. Make sure the thermocouple and laser beam are at the same level but keep the thermocouple out of the path of the laser.
4. Determine the temperature of maximum light scattering. You can raise and lower the temperature several times if necessary, using hot water, cold water and ice, to locate the phase transition precisely.
6. Repeat steps 2-5 for the other solutions to obtain temperature versus mole fraction data.
7. Plot your data as you collect each transition temperature to determine whether a data point should be repeated or a solution of intermediate mole fraction should be studied.
8. Construct the phase diagram on a temperature *versus* mole fraction plot. Add the two 25°C points calculated from the results of part I. Report the upper critical temperature and the critical mole fraction. Compare them to values from the literature.

References

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