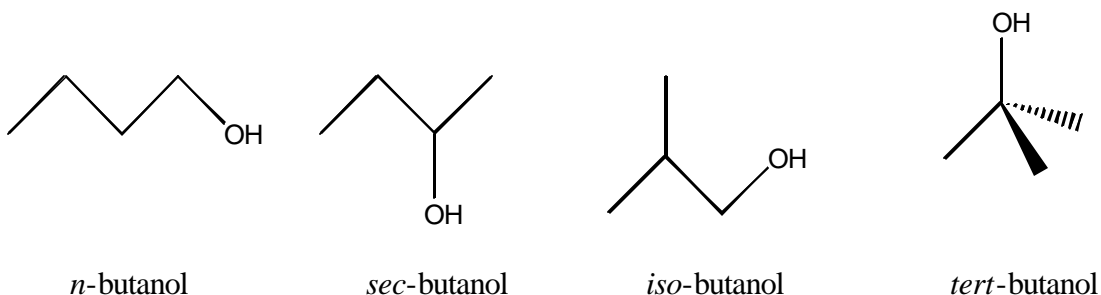


Experiment 1

Mutual Solubility of Liquids in a Binary Two-Phase System

As chemists, we've become familiar with the expression "like dissolves like". In separations lab, you've taken advantage of this to prepare solvent mixtures for chromatographic analyses. You're probably also familiar with the corollary, "dissimilar substances don't mix". Oil and water separate in a salad dressing. Many solvent mixtures that are useful for the purification of organic compounds exhibit limited mutual solubility in one another. This property is required of solvents used for liquid-liquid extraction and counter-solvent precipitation. The mid-range alcohols, C4-C6, exhibit limited mutual solubility behavior with water. To understand why, we need to look at their structure, and the types of interactions with water this structure give rise to.

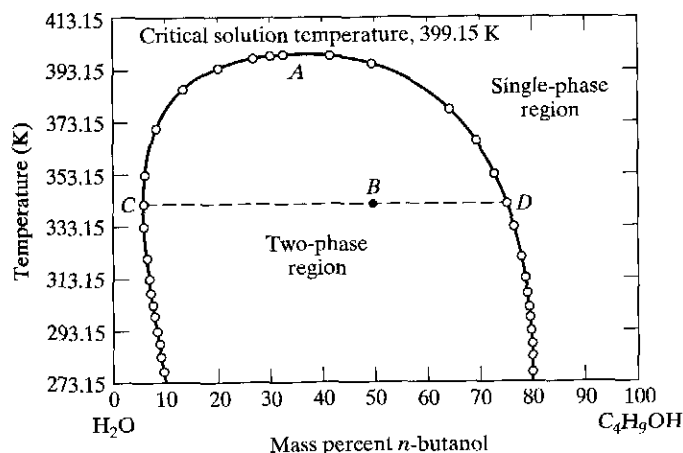
The lower alcohols - methanol, ethanol and the two propyl alcohols - are completely miscible in water. Any composition of alcohol and water will give rise to a homogeneous solution. There are four isomers of butanol. They are depicted below. Of these isomers, *tert*-butanol is soluble in water. It also exhibits homogeneous solutions at any composition. The other three butyl alcohol isomers give rise to two-phase mixtures over most of the composition range. The more dense water-rich phase contains some alcohol. Similarly, the less dense alcohol-rich phase has some water dissolved in it. The proportion of water to alcohol in the two phases is dependent on temperature, but not the overall composition of the mixture. Provided two phases are present, the equilibrium composition of each phase will remain constant at a particular temperature. The variation of the equilibrium composition with temperature is depicted by a phase diagram. The phase diagram for *n*-butanol/water is given in the figure on the next page.



The phase diagram for *n*-butanol is typical for the three partially miscible C4-alcohols. At a given temperature (represented by the dotted line CD) the mixture will separate into two phases whenever the overall composition lies within the phase envelope. As an example, consider the 50 mass % mixture represented by point B. The two layers that form will have compositions represented by point C (water-rich lower layer) and point D (alcohol-rich upper layer). Any mixture represented by a point on the dotted line will phase separate into a top layer with composition D and a bottom layer with composition C. If the temperature is raised, or the mixture is diluted in either component, the two phases will coalesce to give a single phase. Conversely, cooling a homogeneous mixture into the two-phase region causes the solution to become cloudy. This "cloud point" can be used to map the locus of equilibrium compositions. Cooling a

solution with a composition given by point A will cause it to exhibit a blue haze. This is known as critical opalescence and occurs slightly above the critical solution temperature. The critical solution temperature for the *n*-butanol/water system is 126 °C. Below this temperature the mixture phase separates, provided the overall composition lies within the phase envelope. The phase envelope is formed by the locus of equilibrium compositions for the water-rich (left) and alcohol-rich (right) phases.

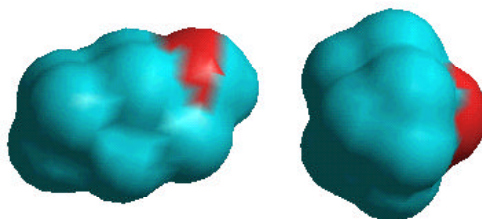
Phase Diagram for the *n*-Butanol/Water Mixture



The mixing of two components to form a homogeneous solution is driven by the increase in entropy (randomness) of the components in the solution relative to that of the individual, pure components. This increase in entropy is referred to as the entropy change of mixing, ΔS_{mix} . If the bonding interactions in the mixture are weaker than those of the pure components, the mixing process will be endothermic. The energy required to weaken the bonds during the endothermic mixing process is given by the enthalpy change of mixing, ΔH_{mix} . Both ΔS_{mix} and ΔH_{mix} are positive for endothermic mixing. Phase equilibrium is established when these effects balance each other.

The phase diagram for the *n*-butanol/water mixture, given in the figure above, is not symmetrical. Water is more readily dissolved in *n*-butanol than is alcohol in water. This is partly due to the smaller size of the water molecule, and partly due to the energetics of the mixing process. Hydrogen bonding in water is stronger than that in the alcohols. When *n*-butanol and water are mixed, water molecules form strong polar and hydrogen bonds with the hydroxyl group of the alcohol. However, the hydrocarbon portion of the molecule hardly interacts with water at all. In the case of ethanol, or *tert*-butanol, the gain in bonding at the hydroxyl end of the molecule offsets the loss in bonding at the hydrocarbon end of the molecule. For *n*-butanol, and alcohols with even larger hydrocarbon "tails", the balance is shifted to the loss of bonding at the hydrocarbon end. The effect is not the same if the alcohol is dissolved in water, or if water is dissolved in the alcohol. Owing to the stronger hydrogen bonds in water, water molecules react to the presence of the hydrocarbon end of an alcohol molecule by forming a structured cage around it. This structure is similar to that found in ice crystals. Since some of the water molecules become structured, or ordered, the overall entropy of mixing is diminished. This phenomenon, unique to water, is called the hydrophobic effect. The magnitude of the

hydrophobic effect depends roughly on the surface area of the hydrocarbon group. Therefore, *n*-propanol is water soluble and *n*-butanol is only partially soluble in water. The solvent accessible surfaces of *n*-butanol and *tert*-butanol are given below. Although different in shape, the surface area of these alcohols is roughly the same. There must be another factor at play. As the name indicates, *tert*-butanol is a tertiary alcohol. *n*-Butanol is a primary alcohol. Perhaps the position of the hydroxyl group plays some role in directing how the water molecules are arranged around the alcohol.



Solvent accessible surfaces of *n*-butanol (left) and *tert*-butanol (right).
Oxygen is the darker region to the right of each molecule.

Since all the C₄ alcohols have roughly the same solvent accessible surface area we might hypothesize that, based on the known behavior of *tert*-butanol and *n*-butanol, water solubility increases from a primary to a secondary to a tertiary placement of the hydroxyl group. If this is the case, *iso*-butanol (also a primary alcohol) should have similar solubility characteristics to *n*-butanol. These ideas are conveyed by the following hypothesis statements.

Hypothesis Statements:

- 1) The room temperature solubility of *sec*-butanol in water is greater than that of *n*-butanol.
- 2) The room temperature solubility of *iso*-butanol in water is the same as that for *n*-butanol.

A hypothesis is always a statement that can be demonstrated to be true or false within the confidence limits that the data will allow. To test these hypotheses will require that the mutual solubility of *n*-butanol, *iso*-butanol and *sec*-butanol with water be measured precisely. To accomplish this, you will use a variation of the volumetric technique proposed by Hill¹. The accuracy of the method will be tested using the *n*-butanol/water system, for which equilibrium composition data is available. You will then use the statistic for the difference between two means to determine whether these hypotheses can be accepted or rejected.

You will prepare a series of water/alcohol mixtures that exhibit two phases. The bottom, water-rich phase will be designated as phase 1. The top, alcohol-rich phase will be designated as phase 2. During the experiment you will vary the mass of alcohol and record the volume changes for the resulting upper and lower layers.

The mass of water in the centrifuge tube, m_w , is given by the relationship:

$$m_w = C_{w1}V_1 + C_{w2}V_2 \quad (1)$$

where C_{w1} represents the mass concentration of water in phase 1 (lower). Similarly, the total mass of alcohol in the centrifuge tube is given by:

$$m_{alc} = C_{alc1}V_1 + C_{alc2}V_2 \quad (2)$$

Solving equations (1) and (2) for the volume of the lower phase, V_1 , and the upper phase, V_2 , gives:

$$V_1 = \frac{m_w C_{alc2}}{C_{w1} C_{alc2} - C_{w2} C_{alc1}} - \frac{m_{alc} C_{w2}}{C_{w1} C_{alc2} - C_{w2} C_{alc1}} \quad (3)$$

$$V_2 = \frac{-m_w C_{alc1}}{C_{w1} C_{alc2} - C_{w2} C_{alc1}} + \frac{m_{alc} C_{w1}}{C_{w1} C_{alc2} - C_{w2} C_{alc1}} \quad (4)$$

Consider an experiment for which the mass of water, m_w , is held constant while varying the mass of alcohol. For this case, equations (3) and (4) have the form:

$$V_1 = \alpha_1 + \beta_1 m_{alc} \quad \text{and} \quad V_2 = \alpha_2 + \beta_2 m_{alc} \quad (5)$$

Where

$$\mathbf{a}_1 = \frac{m_w C_{alc2}}{D} \quad \mathbf{b}_1 = \frac{-C_{w2}}{D} \quad (6)$$

$$\mathbf{a}_2 = \frac{-m_w C_{alc1}}{D} \quad \mathbf{b}_2 = \frac{C_{w1}}{D} \quad (7)$$

Here D represents the denominator of expressions (3) and (4).

Expressions (6) and (7) give a system of four equations for the four compositions C_{alc1} , C_{alc2} , C_{w1} and C_{w2} . The bad news is, the equations aren't linear. The good news is; you don't have to solve them. Instead we are interested in the mass fraction of alcohol in the two layers, f_{alc1} and f_{alc2} . These are given by:

$$f_{alc1} = \frac{C_{alc1}}{C_{alc1} + C_{w1}} \quad f_{alc2} = \frac{C_{alc2}}{C_{alc2} + C_{w2}} \quad (8)$$

By combining expressions (6) and (7), we can solve for the mass fractions in terms of the slopes and intercepts of V vs. m_{alc} . The resulting expressions are:

$$f_{alc1} = \frac{\mathbf{a}_2}{\mathbf{a}_2 - m_w \mathbf{b}_2} \quad (9)$$

$$f_{alc2} = \frac{\mathbf{a}_1}{\mathbf{a}_1 - m_w \mathbf{b}_1} \quad (10)$$

The mass fraction of water in a layer is simply obtained by $1-f_{alc}$ for that layer.

Experimental:

Reagents:

n-butanol (1-butanol)
iso-butanol (2-methyl, 1-propanol)
sec-butanol (2-butanol)
deionized water

Main Apparatus:

15 mL graduated centrifuge tubes
Clean silicone stoppers for tubes
Digital Balances
Digital Thermometer
Transfer Pipets
2 100-mL beakers
2 500-mL beakers

Procedure:

- 1) Set up a constant temperature bath using a 500-mL beaker. Water is a better thermal reservoir than air. After it equilibrates, determine the temperature of the bath.
- 2) Establish a standard temperature for the lab. The digital thermometers need to be referenced to that standard.
- 3) Obtain 50 mL of deionized water and 15 mL of *n*-butanol and allow them to equilibrate to room temperature. Record their temperatures.
- 4) Add ~5 mL of deionized water to a clean centrifuge tube. Then add 5 mL of *n*-butanol to the tube and mix well. Record your visual observations. Using the digital thermometer, determine the temperature of the top and bottom phases.
- 5) Place the tube in your temperature bath and determine the time required to equilibrate the mixture.
- 6) Gently warm up the equilibrated mixture; then cool the newly equilibrated mixture. Record your observations at both temperatures.
- 7) Record the mass of a clean, dry centrifuge tube with its stopper. **Do not clean the centrifuge tube with soap.** Soap residue will prevent you from obtaining a well-defined interface between the water-rich and alcohol-rich layers.
- 8) Start with 4 mL of deionized water in the centrifuge tube. Accurately determine the mass.
- 9) Add about 1 mL of *n*-butanol to the centrifuge tube. Mix thoroughly, allowing gas to escape as needed.

- 10) Allow the system to equilibrate in the water bath and record the volume at the lower (1) and upper (2) meniscus.
- 11) Record the mass of the tube and the temperature of the water/alcohol mixture.
- 12) Repeat procedures 9-11, using 0.5-mL increments until you have filled the centrifuge tube to the top graduation (or until you lose clearance with the stopper).
- 13) Repeat steps 7-12 using *iso*-butanol.
- 14) Repeat steps 7-12 using *sec*-butanol.

The assignment should be electronically submitted as a Word document to me at tdasch@rit.edu. Include your Excel sheet so that I can find potential calculation errors. However, all questions **must** be answered in the Word document. Be sure to include appropriate units and proper significant figures with all quantitative information.

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Mutual Solubility of Liquids in a Binary Two-Phase System

- 1) In several paragraphs, describe the experiment. in a summary paragraph. Include the goal of the experiment, the techniques used to address the problem statement, and the theoretical background that is needed to interpret the results. DO NOT copy directly out of the handouts. I'm interested in your ability to understand the experiment.
- 2) In paragraph form, give a brief description of your procedure. Don't give a recipe. Rather, describe the experiment that you did in a way that will be intelligible to you six months from now. Include any observations or precautions that you took.
- 3) Describe your observations and results to steps 4-6 of the procedure. Is the mixing process exothermic or endothermic? Was there a temperature gradient in the cylinder? Discuss this. What was the equilibration time? Was it different for the temperature than for the phase separation?
- 4) Make a table of the mass/volume/temperature data for the lower and upper phase for each of the three alcohol/water mixtures. Be sure to label these tables. I should be able to tell at a glance what all the information in the table is. Be sure to include the adjusted temperature and the initial mass of water.
- 5) Prepare plots of the volume data as a function of the mass of alcohol added to the centrifuge tube. Include the data for the lower phase volume, V_1 , and the upper phase volume, V_2 , on the same plot. You should have three plots in all, one for each alcohol/water mixture. Only use volume data for mixtures where two phases were present. Each plot should have a title, appropriate labels, and a caption identifying the information that is being presented.
- 6) Use the Regression analysis tool in Excel to determine the: 1) slope, 2) intercept, 3) standard error of the slope and intercept, and 4) the standard error of regression.
- 7) Using equations (9) and (10), determine the mass fraction of alcohol in the top and bottom layers for the three alcohol/water mixtures.

- 8) Expressions (9) and (10) both have the form $f = \alpha/(\alpha - m\beta)$. To determine the error associated with the mass fractions, ϵ_f , we need to take the sum:

$$e_f^2 = \left(\frac{\partial f}{\partial a}\right)_{b,m}^2 e_a^2 + \left(\frac{\partial f}{\partial b}\right)_{a,m}^2 e_b^2 + \left(\frac{\partial f}{\partial m}\right)_{a,b}^2 e_m^2$$

where ϵ_α , ϵ_β , and ϵ_m are the standard errors of the intercept, slope and mass of water, respectively. The partial derivatives give an indication of how sensitive the overall error is to errors in the particular variable. Show that the derivatives have the form:

$$\left(\frac{\partial f}{\partial a}\right)_{b,m} = \frac{-mb}{a^2} f^2 \quad \left(\frac{\partial f}{\partial b}\right)_{a,m} = \frac{m}{a} f^2 \quad \left(\frac{\partial f}{\partial m}\right)_{a,b} = \frac{b}{a} f^2$$

- 9) Determine the confidence limits for f_{alc1} and f_{alc2} for the *n*-butanol/water system using ϵ_f as the standard error for the mass fraction. Be sure to use the correct slopes and intercepts when doing the calculation. The mass % of *n*-butanol in *n*-butanol/water for various temperatures is given in the following table. Use the 95% confidence limits of your *n*-butanol/water data to discuss the accuracy of the experimental method. What are potential sources of systematic errors. Argue whether these causes would lead to positive or negative deviations in the results. Refer to your responses to question (3) to help make your case.

Temp (°C)	n-butanol	
	% alc 1	% alc 2
0		
5	9.55	80.38
10	8.91	80.33
15	8.21	80.14
20	7.81	79.93
25	7.35	79.73
30	7.08	79.38
35	6.83	78.94
40	6.6	78.59
50	6.46	77.58
60	6.52	76.38
70	6.73	74.79
80	6.89	73.53

- 10) The 95% confidence limits for f_{alc} indicate the precision of the result. The precision can be improved by reduces the effect of random errors. Give some sources of random error in this experiment, and suggest improvements to reduce them.

11) Now we need to test the hypotheses given in the problem statement. Recall, these were:

The room temperature solubility of *sec*-butanol in water is greater than that of *n*-butanol.

The room temperature solubility of *iso*-butanol in water is the same as that for *n*-butanol.

To do this you will have to calculate the two differences

$$f_{\text{alc1}}(\textit{sec}\text{-butanol}) - f_{\text{alc1}}(\textit{n}\text{-butanol})$$

$$f_{\text{alc1}}(\textit{iso}\text{-butanol}) - f_{\text{alc1}}(\textit{n}\text{-butanol})$$

and establish whether the respective difference is significant at the 95% confidence level. Start by calculating the standard error for $f_{\text{alc1}}(\textit{sec}\text{-butanol})$ and $f_{\text{alc1}}(\textit{iso}\text{-butanol})$. Determine the pooled variance, s_p^2 , for the two differences. The sample variances for the individual f_{alc} -values are obtained from the standard errors by $s^2 = n\varepsilon^2$. Here s^2 is the sample variance, n is the number of data points used to determine a particular f_{alc} -value, and ε is the standard error of the particular f_{alc} -value. Finally, determine the 95 % confidence limits of the differences, $\lambda = t_{0.05} s_p (1/n_1 + 1/n_2)$. Based on these confidence limits, discuss whether the hypotheses given in the problem statement are true or false.

12) Write an abstract for this experiment. Include an introductory statement, a concise statement of the work that was done, significant numerical results with confidence limits, and a comparison to results found in the literature. Think about the abstract as an advertisement for your work. It should stand on its own, yet entice the reader to look further.