MISIBILITY

INTRODUCTION

Molecular polarity is a continuum with completely nonpolar molecules at one end to completely polar (almost “ionic”) molecules at the other end. Nonpolar molecules can be in two classes: Molecules with negligible differences in atom electronegativity, and, therefore, no bond dipoles, and molecules with symmetrical bond dipoles that cancel each other out. Polar molecules encompass a broad class of molecules, varying by their extent of polarity. In these molecules, one or more bond dipoles create a partial separation of charges resulting in an overall bond dipole.

How does polarity difference affect intermolecular forces when two different chemicals interact to form a solution? What does “like dissolves like” mean? When dealing with a solid solute and a liquid solvent, the solute dissolves when the molecules of both are similar enough in polarity. For example, water dissolves other polar molecules (sucrose C₁₂H₂₂O₁₁, urea H₂NC(O)NH₂, etc.), ionic compounds (NaCl, Fe(NO₃)₃, etc.), and Arrhenius acids (citric acid H₃C₆H₅O₇, potassium hydrogen phthalate KHC₈H₄O₄ etc.). Observe the hydrogen atoms bound to oxygen and nitrogen atoms and carbon atoms bound to oxygen atoms in Figure 2. All of these polar bonds are capable of ion-dipole, hydrogen bonding, and/or dipole-dipole forces that result in the dissolution of the solid to create a homogeneous solution.
Nonpolar liquids also dissolve nonpolar solids according to the same “like dissolves like” adage. For example, nonpolar heptane (C\textsubscript{7}H\textsubscript{16}) dissolves nonpolar hydrocarbons, like long chain fatty acids (trans-oleic acid CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{7}CH=CH(CH\textsubscript{2})\textsubscript{7}COOH) and cholesterol. As seen in Figure 3, each has one oxygen atom bound to a hydrogen atom. However, this polar bond is a very small part of the overall molecule, so dispersion forces are assumed to be the main intermolecular interactions. Again, because of the similarity in intermolecular interactions, the solid is able to dissolve into the solvent forming a homogeneous solution.

**Figure 2.** Polar Molecules, & Acids: Species Soluble in Water (a Polar Solvent)

**Figure 3.** Large Hydrocarbons: Species Soluble in Heptane, CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3} (a Nonpolar Solvent)
Regardless of polarity, when a solid dissolves into a liquid to form a homogeneous solution the 

solid is the **solute** and the liquid the **solvent**. The solute is, therefore, **soluble** in the solvent. This idea of solubility can be extended to the interactions between two liquids. If two liquids with similar polarities (and, therefore, similar intermolecular interactions) are combined, the liquids are said to be **miscible** with each other because the will mix to form a homogeneous solution. Examples of solutions created with miscible liquids include: Gasoline is a mixture of many organic solvents such as benzene, toluene, xylenes, and others. Alcoholic drinks contain ethanol and water. Molten copper and zinc are completely miscible - resulting in a solid alloy (brass) once cooled.

The qualitative treatment of “like dissolves like” explained above is based on assessing the 
polarity of the molecular structure to predict solubility and miscibility. To further broaden the 
understanding of solution formation, the thermodynamics of the process must be understood. 
According to the equation for **free energy**:

\[
\Delta G_{\text{soln}} = \Delta H_{\text{soln}} - T\Delta S_{\text{soln}}
\]  

(1)

solution formation is spontaneous (occurs) when \(\Delta G_{\text{soln}} < 0\) (\(\Delta G_{\text{soln}}\) is negative). **Entropy** always increases with solution formation, in other words, \(\Delta S_{\text{soln}} > 0\) (\(\Delta S_{\text{soln}}\) is **always** positive). So the 
spontaneity of solution formation (whether or not a solution will form) depends on the sign of the 
enthalpy of solution, \(\Delta H_{\text{soln}}\). Applying Hess’ Law, \(\Delta H_{\text{soln}}\) is the sum of 3 individual enthalpies 
(\(\Delta H_1 + \Delta H_2 + \Delta H_3\)): \(\Delta H_1\), the energy added (+\(\Delta H\)) to break intermolecular forces between 
solvent molecules (or the molecules of the first liquid); \(\Delta H_2\), the energy added (+\(\Delta H\)) to break 
termolecular forces between solute molecules (or the molecules of the second liquid); \(\Delta H_3\), the 
energy released (-\(\Delta H\)) from the attraction between solvent and solute molecules (or between 
molecules of the first and second liquids). If \(\Delta H_3 > \Delta H_1 + \Delta H_2\), the solution formation is 
exothermic and since \(\Delta S_{\text{soln}}\) is always positive, the solution forms. If \(\Delta H_3 < \Delta H_1 + \Delta H_2\), solution 
formation is **endothermic**. In this case, solution formation occurs if -\(T\Delta S_{\text{soln}} > +\Delta H_{\text{soln}}\). 
Therefore, large entropies and/or high temperatures favor solution formation.

This lab uses the **MORE** (Model, Observe, Reflect, and Explain) approach.

**Model:** Your prelab assignment is to use your current knowledge to construct a nano- and/or 
macroscale understanding of the chemistry you are about to perform.

**Observe:** While completing the procedures below, make detailed observations thinking about 
the model you created in the prelab.

**Reflect & Explain:** Do your observations prove or disprove your model? Construct a short 
written report based on your observations that supports or refutes your initial model.
Make sure you watch the videos on the course website and read the documents to prepare for the demonstrations below each week. Everyone will have to present at least one topic by the end of the quarter. The demonstrations should be short (>1 min) and will be graded. Before starting the experiment, the TA will ask you to do a quick demonstration or talk-through one of the following:

1) Grab the correct glassware off the shelf: a volumetric flask and volumetric pipet
2) Show how to use a volumetric flask, specifically: how do you get to the correct volume you want?
3) How to use a volumetric pipet, specifically: how to draw liquid into the pipet, and how do you get the correct volume you want?
4) How to use a separatory funnel, specifically: How do you clamp and set up the separatory funnel before adding the liquids?
5) How to use a separatory funnel, specifically: How and when do you vent a separatory funnel?
6) How to use a separatory funnel, specifically: How do you drain liquid from the separatory funnel?

**SAFETY PRECAUTIONS**

Safety goggles, aprons, and gloves must be worn at all times in the laboratory. Heptane, acetone, ethyl acetate, and ethanol are flammable and harmful by inhalation, ingestion, and when in contact with skin. Any container holding either heptane, acetone, or ethyl acetate should be capped when not in use to prevent evaporation of the solvents, as they are harmful when inhaled. Heptane and acetone solutions must be placed in appropriate waste bottles and can NEVER be poured down the drain. Report all spills, accidents, or injuries to your TA.

**PROCEDURE**

*Record all data in your ELN. Chemical and equipment tables and procedures are still required.*

**Part A: Miscible Liquids: Are Volumes Additive?**

A number of solutions will be prepared from two miscible liquids. Actual solution volumes will be compared to expected volumes that are calculated from the densities of the pure liquids and the measured masses of the solutions. The conservation of mass law is obeyed: the masses of the individual liquids add up to the mass of the combined solution. But is volume conserved?
In other words, when 10.00 mL of water is added to 10.00 mL of alcohol, is the volume of the resulting solution greater than, equal to, or less than 20.00 mL?

If the volumes of two different chemicals are additive, the sum of each chemical’s volume will be equal to the resulting solution volume ($V_{\text{actual}} = V_{\text{additive}} = V_{\text{water}} + V_{\text{EtOH}}$). However, if the volumes are not additive, the solution volume will not equal the sum of the component volumes ($V_{\text{actual}} < V_{\text{additive}}$ or $V_{\text{actual}} > V_{\text{additive}}$).

**Model.** *(Prelab)*

1. Draw a visualization showing 5 molecules of H$_2$O interacting with 5 molecules of EtOH. Also, provide a short (no more than 3 sentences) written argument supporting the choices you made in the drawing.

2. Draw a visualization showing 5 molecules of acetone interacting with 5 molecules of heptane. Also, provide a short (no more than 3 sentences) written argument supporting the choices you made in the drawing.

**Observe.** *(Procedure)*

1. **Work alone.** Weigh an empty, dry 10-mL volumetric flask and stopper. Record the mass to the nearest milligram (3 decimal places).

2. Fill the 10-mL volumetric flask to the calibration mark with deionized water. Stopper and weigh. Pour the water down the drain (for this step only).

3. Pour about 100-mL of ethanol (EtOH) into a clean, dry beaker. Using a disposable pipet, transfer enough EtOH from the beaker into the 10-mL volumetric flask to fill the flask to the calibration mark. Stopper and weigh the filled volumetric flask. When finished, pour contents into a 1 L beaker, to treat at the end of the experiment.

4. Using volumetric pipets prepare a "15+5" solution of EtOH and water (15.00-mL of EtOH plus 5.00-mL of water) in an Erlenmeyer flask. Mix thoroughly.

5. Rinse the volumetric flask with a few mL of the solution then fill the 10-mL volumetric flask exactly to the mark with the prepared solution. Stopper and weigh the filled flask. When finished, combine the contents in the 1 L beaker from step 3.
6. Repeat the above procedure, measuring and weighing the following EtOH-DI water solutions: 10+5, 10+10, 5+10, 5+15, 10+1, and 15+2. Use a graduated pipet for smaller volumes. When finished, triple the volume of solution in the 1 L beaker with water and pour down the drain. If an aqueous solution is 24% or less ethanol it poses no environmental threat and can be poured down the drain.

7. Repeat the above procedure, measuring and weighing one of the following Heptane-Acetone solutions: heptane only, acetone only, 15+5, 10+5, 10+10, 5+10, 5+15, 10+1, and 15+2. (Your TA will assign you one solution.) Solutions should be kept tightly cap unless in use to prevent the formation of harmful organic fumes in the lab. Share your data with your lab mates by writing the solution made, the mass of the volumetric flask and solution, and the mass of the empty, dry volumetric flask on the lab’s whiteboard or an Excel spreadsheet set up by your TA. You will need all students’ data for the post-lab questions. Solutions should be placed in the Acetone-Heptane waste bottle in the fume hood.

8. Return volumetric pipets and flasks to their original location.

Observe. (Calculations). This work can be done after lab. Show one sample calculation for #1-5 below and then enter all data into Excel or Numbers. The spreadsheet should be attached to your ELN with a screen shot of the results table. Remember to express the results with the correct number of significant figures.

1. For pure water and pure ethanol, calculate the
   a. Mass of water in the 10 mL volumetric flask.
      \[ m = \text{mass of flask w/ water} - \text{mass of empty flask} \]

   b. Density of the water (\( D_{\text{water or EtOH}} \)) in the 10 mL volumetric flask.
      \[ D_{\text{water}} = m / \text{flask volume} \]

2. For the ethanol-water mixtures, calculate the
   a. Mass of each mixture in the 10 mL volumetric flask.
      \[ m_{\text{vol}} = \text{mass of flask w/ liquid} - \text{mass of empty flask} \]

   b. Density of each mixture in the 10 mL volumetric flask.
      \[ D_{\text{mix}} = m / \text{volumetric flask volume} \]
c. Mass of each mixture in the \textit{Erlenmeyer flasks}.
\[ \text{m}_{\text{erlenmeyer}} = (V_{\text{EtOH}}D_{\text{EtOH}} + V_{\text{water}}D_{\text{water}}) \]

d. "\textit{Actual volume}" of each mixture in the \textit{Erlenmeyer flasks}.
\[ V_{\text{actual}} = \frac{\text{m}_{\text{erlenmeyer}}}{D_{\text{mix}}} \]

e. "\textit{Additive volume}" of the ethanol-water mixtures in the \textit{Erlenmeyer flasks}.
\[ V_{\text{additive}} = V_{\text{water}} + V_{\text{EtOH}} \]

3. Calculate the percent change in volume for all mixtures and pure water and ethanol. Indicate whether the actual volume is decreasing or increasing with + or − signs.
\[ \% \Delta V = \frac{(V_{\text{actual}} - V_{\text{additive}})}{V_{\text{additive}}} \times 100 \]

4. Calculate the mole fraction of ethanol (\( \chi_{\text{EtOH}} \)) for all mixtures and pure water and ethanol.
\[ \chi_{\text{EtOH}} = \frac{\text{moles}_{\text{EtOH}}}{\text{moles}_{\text{EtOH}} + \text{moles}_{\text{water}}} = \frac{[(V_{\text{EtOH}} x D_{\text{EtOH}}) / MW_{\text{EtOH}}]}{[(V_{\text{EtOH}} x D_{\text{EtOH}}) / MW_{\text{EtOH}}] + [(V_{\text{water}} x D_{\text{water}}) / MW_{\text{water}}]} \]

5. Plot percent change in volume versus the mole fraction of organic solvent. Make sure to put the independent variable on the x-axis. Draw a solid smooth curve connecting the data points.

6. Repeat the above calculations and create the plot for the data collected for heptane+acetone mixtures. (Calculate the mole fraction of ethanol (\( \chi_{\text{heptane}} \))). Only a table and plot are needed, sample calculations do not need to be shown.
Part B: Immiscible Liquids: Extraction of a Solute.

Two immiscible liquids (ethyl acetate and water) will be used to perform a liquid-liquid extraction with the red dye, Allura Red AC (a solid at room temperature). The red dye will become a solute in the liquid it has the most affinity for – like dissolves like.

Model. (Prelab)

Draw a visualization with 5+ molecules of water and 5+ molecules of ethyl acetate that demonstrates what immiscible means. Draw a macroscopic (not molecular level) visualization of these two liquids in a separatory funnel. Explain all the components of the drawing and indicate how and predict which the layer Allura Red AC dissolves in.

Observe. (Procedure)

9. Obtain a 60 mL sep funnel and stopper. Make sure the stopcock is closed. Suspend the sep funnel in an iron ring or clamp in place. (Figure 1)
10. Stoppers tend to get stuck in the funnel – avoid getting the ground glass surfaces wet. To do this use a funnel to pour ~20 mL H₂O and ~20 mL ethyl acetate. Observe which layer is on the bottom and which layer is on the top (Figure 2). (If you aren’t sure, add ~ 1 mL H₂O by plastic pipet and observe which layer it adds to.)
11. Add one drop of food coloring. Note where the color initially travels to without mixing.
12. Stopper the sep funnel.
13. Remove the sep funnel from the iron ring or clamp.
   Hold stopper and stopcock tightly. Pressure may build up during the next step.
14. Invert the sep funnel (Figure 3). Point the stem of the funnel away from yourself and others! Make
sure the liquid has drained down away from the stopcock, then slowly open the stopcock (Figure 4). You may hear a “woosh” as the pressure is released. Close stopcock.

15. Shake the funnel gently, then repeat step 13.

16. Repeat steps 13 and 14 until no more gas escapes.

17. Put the sep funnel back in the iron ring.

18. Observe which layer the food coloring has added to.

19. Remove the glass stopper. Otherwise the funnel won’t drain – why?

20. Open the stopcock slowly and let the bottom layer drain off into a 125 mL Erlenmeyer flask (Figure 5).

21. Close the stopcock, swirl the funnel gently to see if any more of the bottom layer forms. If so, collect it. If not, assume you got it all in the flask (Figure 6).

22. Drain the top layer into another 125 mL Erlenmeyer flask.

23. Discarding solutions: Show the TA your ethyl acetate layer. Your TA will instruct you what to do with it. Only after this, pour your aqueous layer down the drain.

Reflect and Explain. (Discussion and Conclusion)

Part A. Is $V_{\text{actual}} >, <,$ or $= V_{\text{additive}}$ for the EtOH / water solutions? What about the heptane / acetone solutions? How does these results change your initial visualizations? Redraw them if necessary. Write a brief paragraph using chemical theory to explain your observations and supporting your conclusions.

Part B. In what way do your observations change your model? Did the dye go to the layer you predicted? Explain why the dye went into the layer that it did. Redraw any visualizations if necessary.