

Experiment 1

SOLVENT POLARITY AND MISCIBILITY

Fig. 1-1



carbonated water

Test Topics

Molecular polarity, solubility. Please be sure to read the *Preface* before continuing.

Discussion

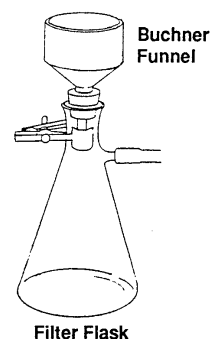
Your exciting adventure into organic chemistry begins with an exploration of the miscibilities of organic solvents. It is extremely important to recognize that a knowledge of solvent properties enhances the ability of an organic chemist to achieve desired goals in a timely manner. The selection of solvents plays a major role in several separation and purification techniques including recrystallization, extraction and chromatography. In addition, solvents can strongly influence rates of reactions and product yields. The choice of solvent is a complex matter and includes consideration of many physical properties such as boiling point, density, cost and toxicity. Perhaps most important is a consideration of the solubility of compounds of interest (reagents, products and other solvents) in the solvent. Even the temperature dependence of solubility is important. While some predictions are possible by comparing polarities of compounds, the best way to acquire the ability to choose the optimum solvent comes from insight gained from experience. This experiment has been designed to provide some of the insight needed to choose solvents wisely and in a timely manner.

“Like dissolves like” is a simple phrase often used to predict solubilities. “Like” usually refers to polarity. Unfortunately, there is no universally accepted method for ranking polarities. Dipole moments, dielectric constants and empirically derived parameters are used with varying degrees of success. You have probably used electronegativity values to predict bond polarities. By considering Lewis structure geometries and bond polarities, it is possible to predict molecular polarities. Consider a bottle of carbonated soda as illustrated in the upper right. Although carbon dioxide has polar carbon-oxygen bonds, the linear structure predicted by the Lewis structure and VSEPR theory and verified experimentally leads to the prediction that carbon dioxide should be non-polar and have low solubility in very polar water. This prediction is realized when a bottle of carbonated soda is opened and the carbon dioxide begins to escape from the water due to the low solubility of carbon dioxide in water (1.5 g/L or 0.034 M at 25°C and 760 mm CO₂). At this point, it would be to your advantage to do *Exercise 2* which reviews the drawing of Lewis structures and prediction of molecular polarities.

Unfortunately, electronegativity values have significant limitations that reduce their predictive power. For instance, the carbon-iodine bond behaves in substitution reactions as though it is polar with a partial negative charge on the iodine and a partial positive charge on the carbon. Some electronegativity scales predict the opposite polarity. Electronegativities alone also do not explain why ammonia hydrogen bonds but hydrogen chloride does not. Lacking a definitive method for comparing solvent polarity, this text uses

an empirical parameter developed by Christian Reichardt derived from shifts of the energy of absorption spectra. **Table 2** in **Appendix B** and the very abbreviated table that follows on this page list many solvents arranged according to increasing values of solvent polarity as determined by the magnitudes of spectral shift. It should be recognized that this measure of solvent polarity is only presented as a guide. In fact, you should notice in **Appendix B** that eluant strength is another indication of solvent polarity but only very roughly correlates with the spectral parameter. As indicated earlier, the best way to choose a solvent will come from the insight you gain from experience.

As an example of techniques that involve solvent selection, consider two of the techniques that will be used in early experiments to separate and purify compounds. Recrystallization requires a solvent that will dissolve a compound in a hot solution but has considerably lower dissolving ability at room temperature and lower. The sample is transferred to the solvent. If the solvent has been properly selected, the compound of interest does not dissolve substantially at room temperature. Upon heating it dissolves and then recrystallizes when the solvent is cooled. Ideally, any impurities in the original sample will either not dissolve in the hot solvent and can be filtered out then or more commonly, the impurities stay dissolved when the solvent is cooled. Collection of the sample via vacuum filtration should yield a purer sample.



For the technique of extraction, two immiscible solvents are used with one of the solvents almost always being an aqueous solution. Any compounds dissolved in one of the solvents will distribute themselves between the two solvents. In most cases, compounds strongly prefer one of the solvents over the other. Since it is possible to easily separate the two solvents using a separatory funnel, this method called extraction can separate compounds that are more soluble in aqueous solutions from those that are more soluble in organic solvents.

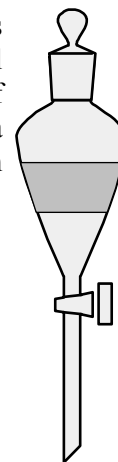


Table 1-1

	<u>Solvent</u>	<u>formula</u>	boil. pt. <u>(°C)</u>	melt. pt. <u>(°C)</u>	density <u>(g/mL)</u>	relative <u>polarity</u>
1.	cyclohexane	C ₆ H ₁₂	80.7	6.6	0.779	0.006
2.	hexane	C ₆ H ₁₄	69	-95	0.655	0.009
3.	toluene	C ₇ H ₈	110.6	-93	0.867	0.099
4.	tetrahydrofuran (THF)	C ₄ H ₈ O	66	-108.4	0.886	0.207
5.	ethyl acetate	C ₄ H ₈ O ₂	77	-83.6	0.894	0.228
6.	ethyl benzoate	C ₉ H ₁₀ O ₂	213	-34.6	1.047	0.228
7.	acetone	C ₃ H ₆ O	56.2	-94.3	0.786	0.355
8.	1-hexanol	C ₆ H ₁₄ O	158	-46.7	0.814	0.559
9.	1-pentanol	C ₅ H ₁₂ O	138.0	-78.2	0.814	0.568
10.	1-butanol	C ₄ H ₁₀ O	117.6	-89.5	0.81	0.586
11.	1-propanol	C ₃ H ₈ O	97	-126	0.803	0.617
12.	ethanol	C ₂ H ₆ O	78.5	-114.1	0.789	0.654
13.	methanol	CH ₄ O	64.6	-98	0.791	0.762
14.	water	H ₂ O	100.00	0.00	0.998	1.000
15.	salt water (10%)		101.8	-6.6	1.071	

Procedure

All miscibility and extraction experiments will be performed in 13 x 75 mm test tubes with 0.5 mL of each solvent. Calibrated pipets will be in test tubes attached to each solvent bottle. Deliver 0.5 mL into the appropriate test tube with the pipet. Add 0.5 mL of the second solvent and attempt to mix the contents of the test tube by holding the test tube firmly between the thumb and forefinger of one hand and striking the bottom of the tube firmly with the forefinger of the other hand. Alternatively, a clean cork or rubber stopper can be inserted into the test tube and the tube can be shaken. To determine partial miscibility, it should help if you transfer 0.5 mL of water and 0.5 mL of hexane to a test tube and keep it as a reference.

1. Determine the miscibility of the first 13 solvents in the table with water and then with water containing 10% by mass sodium chloride. Report the results as miscible, partially miscible or immiscible.
2. For the pairs below, based on your results above, predict if you expect miscibility, partial miscibility or immiscibility. Then test for miscibility.
 - a. methanol, hexane
 - b. ethyl benzoate, hexane
3. Write down your observations about the contents of an aqueous iodine solution. Does iodine appear to be very soluble in water? From Lewis structures, estimate the polarities of water and iodine. Based on the polarities, should iodine be very soluble in water? Add 0.5 mL of a saturated aqueous iodine solution to a test tube and add 0.5 mL of hexane. Shake thoroughly, allow to settle and report your observations.
4. Is it possible with the solvents in the table above to prepare a test tube containing 3 or perhaps 4 phases? If so, do this and demonstrate your results to your instructor. Consider whether the order of addition of the solvents to the test tube makes any difference and whether stirring could cause a loss of one or more phases. Can you think of a way to add color to any of the layers? If you come up with a method, discuss it with your instructor and try it with his/her permission.
5. (With the instructor's approval, do this part with a partner) Thorough mixing is very important in many procedures such as reactions and extractions (recognizing that immiscible liquids will not dissolve in each other). To observe the rate of mixing in the absence of an outside force, perform the following experiment: bring about 100 mL of water to the boiling point and use beaker tongs to carefully pour the water into a 150 mL beaker. Add 100 mL of room temperature water to an identical beaker. Add a drop of food coloring to the top of each beaker in an identical manner. Do not stir or move the beakers but write down your observations about the mixing of the food coloring over the next 30 or so minutes.

References

Baer, C.; Adamus, S. M. *J. Chem. Educ.*, **1999**, 76, 1540.

Passarelli, M. J. *J. Chem. Educ.*, **2009**, 86, 845.

For an interesting extension to this experiment, see: Mueller, S. A.; Anderson, J. E.; Wallington, T. J.; Hammond, R. M. *J. Chem. Educ.*, **2009**, 86, 1045.

Two more miscibility experiments appropriate for the first laboratory day have been published recently at:

Garber, K. C. A.; Odendaal, A. Y.; Carlson, E.E. *J. Chem. Educ.*, **2013**, 90, 755-759.

Shugrue, C. R.; Mentzen, H. H.; Linton, B. R. *J. Chem. Educ.*, **2015**, 92, 135-138.

Prelaboratory Preparation - *Experiment 1*

Before entering the laboratory for this experiment, you should study the *Safety* and *Chemistry Resources* sections of this book. At the beginning of your report in your notebook, you should list the goals of this experiment. Draw structures of all of the compounds in **Table I-1**. Based on polarities of water and iodine that can be predicted from Lewis structures and VSEPR theory, should iodine be very soluble in water? Use a reference or the Internet to determine the solubility of iodine in water. Should iodine be very soluble in hexane? Predict what will happen when hexane is added to the aqueous iodine solution and the solution is mixed. Give reasons for your prediction.

Observations

Report all relevant observations. Include comments on how soluble iodine appears to be in water.

Conclusions

This section should include the following:

1. Were the goals of the experiment achieved? Explain your answer.
2. Were the results on solvent miscibility consistent with solvent polarities? Explain your answer. Explain why the hexane-water test tube was a good reference for the other tests.
3. How would you teach someone about the predicting of solubility?
4. Does salt affect the solubility of organic solvents in water? If so, explain why. During extraction procedures, salt is often added to the aqueous phase before the organic layer is physically separated from the aqueous layer. Explain why.
5. Were your predictions about the miscibility of the pairs, methanol-hexane and ethyl benzoate-hexane correct? Explain your answer.
6. Do your miscibility studies agree qualitatively with the amounts in the *Solubility in H₂O* column in Appendix C?
7. Was your prediction correct about the consequences of adding hexane to the aqueous iodine solution followed by shaking? Were the results consistent with predicted solubilities of iodine in water and hexane? Explain your answer.
8. Discuss the attempt to prepare a 3 or 4 phase mixture.
9. Are the trends of properties (including your observations of miscibility) for the homologous series of alcohols used in this study (methanol to hexanol) consistent with expectations? Explain your answer.
10. List the solvents used that could not be used for an extraction from water and from salt water. Explain your answer.
11. 1 g of urea dissolves in 1 mL of water. Would water be a good solvent for the recrystallization of urea? Explain your answer.
12. Comment on any differences (especially rates) observed for the behavior of the food coloring in hot and room temperature water. Does mixing occur quickly without physical agitation at room temperature? Explain your answer.