Experiment # 10 Using Hansen's Solubility Parameters to Predict the Solubility of Balloons in Different Solvents

This lab was developed by Laura Gray and Lauren Heine, Ph.D., adjunct faculty at Gonzaga University in Spokane, Washington for ENVS 202L: Chemistry of the Environment in 2023. It was inspired by a demonstration video produced by Professor Steven Abbott.[1]

Background

Chemicals that are released into the environment from homes, consumer products, and industrial sources may be detrimental to the health and well-being of humans, plants, and animals. While many of the most toxic substances are regulated by governmental agencies, there is a need to shift the focus from banning the worst offenders to creating and using safer chemicals in the first place. The realization of this need has led to the development of the fields of green chemistry, hazard assessment, risk assessment, alternatives assessment, and design for sustainability. Safer and more sustainable chemicals, materials, and products must also work. There is no point in substituting a safer chemical in a product if it means the product is no longer effective.

Solvents are used to dissolve a multitude of substances such as polymers, plasticizers, nanoparticles and pigments to name a few. They are needed for liquid products such as cleaners and paints. They are also used in chemical manufacturing processes to synthesize materials and sometimes to recycle them. Hansen's solubility parameters (HSP) are numerical estimates that help identify solvents that are "like" in their ability to dissolve substances. These solubility parameters are numerical values used to estimate the degree of molecular interactions between compounds based on their polar, hydrogen bonding, and dispersion parameters. Charles Hansen developed these parameters based in part on the Hildebrand solubility parameters. The robustness of the Hansen Solubility Parameters is increasingly being recognized for the ability of HSP to help scientists avoid many hours of trial and error testing when looking for an effective solvent! Even more impressive is that HSP can be used to find effective mixtures when individual solvents won't do the trick. Hanson's Solubility Parameters can be used to determine mixtures of "bad" solvents that when combined in the correct percentages will successfully dissolve a polymer. This can be a game changer in formulation of alternative, safer and more sustainable solvents.

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[1] https://hansen-solubility.com/HSPiP/video-tutorials.php

In practice, green scientists and engineers looking for a good solvent can start by first identifying one that will work to dissolve the substance of interest - for example, the polymer polyisoprene which is a major constituent of the common balloon. Once a set of effective solvents is identified, then this list can be narrowed down to include the safest options. In this lab, you will use HSP to predict which of a set of 10 candidate solvents are likely to dissolve polyisoprene. Then you will test the solvents and see how well you and HSP predicted the results.

Green Chemistry
Green chemistry was defined by Anastas and Warner (1999) as the design of chemical products and processes to reduce the use and generation of hazardous substances. Table 1 provides a brief outline of some key benchmarks in the development of green chemistry.

Table 1. Brief History of Green Chemistry (modified from ACS History of Green Chemistry)

1960s	1962 – Rachel Carson wrote *Silent Spring*, scientifically documenting how human endeavors were threatening the health of the whole biota. 1969 – Congress passed the National Environmental Policy Act (NEPA) with the goal to "create and maintain conditions under which man and nature can exist in productive harmony."
1970s	1970 – President Nixon established the US Environmental Protection Agency (EPA). 1974 – Congress passed the Safe Drinking Water Act. Late 1970s – Love Canal in Niagara Falls NY brings to light the chemical industries waste management practices contaminating soil and groundwater.
1980s	1980 – The Superfund Act was passed; a significant environmental legislation mandating contamination clean up. The Organization for Economic Co-operation and Development (OECD) was organized involving 30 + countries to address global environmental concerns. 1988 – EPA established the Office of Pollution Prevention and Toxics
1990s	1990 – Pollution Protection Act passed. 1994 – First Symposium "Benign by Design: Alternative Synthetic Design for Pollution Prevention, Chicago. 1995 – EPA with Bill Clinton's support created the annual *Presidential Green Chemistry Challenge Awards*. 1997 – The University of Massachusetts at Boston established the field's first Green Chemistry Ph.D. program. Dr. Joe Breen and Dr. Dennis Hjeresen co-founded the Green Chemistry Institute (GCI) as an independent nonprofit

	dedicated to advancing green chemistry.1997 GCI established the annual Green Chemistry & Engineering Conference. 1998 – Paul Anastas and John C. Warner co-authored the groundbreaking book, *Green Chemistry: Theory and Practice* which outlined the 12 Principles of Green Chemistry.
2000s	2001 – The Green Chemistry Institute became a part of the American Chemical Society 2001 and 2005 – The Nobel Prize in Chemistry was won for research in areas of chemistry that were largely seen as green chemistry, (2001 Knowles, Noyori, Sharpless) (2005 Chauvin, Grubbs, Schrock).

Chemical Hazard Assessment and Alternatives Assessment

Chemical hazard assessment and alternatives assessment complement green chemistry. Green chemistry typically focuses on making new molecules and making molecules in new ways that reduce the use and generation of hazardous substances. However, to identify what is less hazardous, you need to use the tools and practices associated with chemical hazard assessment to compare substances based on their inherent hazards. Alternatives assessment includes chemical hazard assessment but it is more comprehensive. It is a method for including data from other important criteria into decision making such as cost and availability, performance, life cycle impacts and exposure. Some key developments in chemical hazard assessment and alternatives assessment are described below:

- [Globally Harmonized System (GHS) of Classification and Labeling of Chemicals](#). The GHS includes criteria for the classification of health, physical and environmental hazards, as well as specifying what information should be included on labels of hazardous chemicals as well as safety data sheets.
- In 2006, the European Union implemented Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) legislation. REACH is supported by a database that provides a unique source of information on the chemicals manufactured and imported in Europe. It covers their physical properties, hazard classifications, and their uses.
- The International Agency for Research on Cancer (IARC). coordinates and conducts epidemiological and laboratory research into the causes of human cancers and classifies chemicals as carcinogenic to humans, probably carcinogenic to humans, possibly carcinogenic to humanism and not classifiable.
- Tools for chemical hazard assessment continued to evolve and to become integrated into decision making.
  - One of the earliest methods for compiling information on chemical hazards and rating chemicals as a whole based on a suite of hazard endpoints is the [GreenScreen® for Safer Chemicals](#) (GreenScreen). GreenScreen is a publicly

available and transparent set of guidance documents intended to promote the adoption of greener and safer chemicals.

- Pharos is a software platform that incorporates elements of GreenScreen ratings. Pharos is designed to help scientists, researchers and product innovators identify problematic chemicals and assist in finding safer alternatives based on the presence (or absence) of the chemical on authoritative lists of chemicals with specific hazards such as carcinogenicity or toxicity to reproduction.
- Chem*FORWARD* builds on both GreenScreen and Pharos by creating a software platform based on a database of full chemical hazard assessments to help users learn more about chemicals of concern and to find safer alternatives. Methods like GHS and GreenScreen are integrated into ChemFORWARD. What is powerful about ChemFORWARD is that the information is searchable and users can compare chemicals based on their inherent hazards. The hazard assessments are comprehensive because they are done by professional toxicology firms with extensive expertise (Dr. Lauren Heine co-founded and led in development of both GreenScreen and ChemFORWARD.)

Hansen's Solubility Parameters (HSP)

As mentioned above, solvents with similar solubility parameters will be miscible and polymers will dissolve in solvents whose solubility parameters are not too different from their own. The basic principle has been "like dissolves like." More recently, this has been modified to "like seeks like," since many surface characterizations have also been made and surfaces do not (usually) dissolve. Solubility parameters help put numbers into this simple qualitative idea. To use HSP, you need to know:

1. The three Hansen Solubility Parameter values for each solvent and the polymer
2. The algorithm to calculate the Ra values for each solvent/polymer combination
3. How to determine if the solvent is likely to dissolve the polymer or not

The Three Hansen Solubility Parameters include:
1. δD Dispersion or polarizability
2. δP Polarity
3. δH Hydrogen bonding

There are three major types of interaction in common organic materials. The most general are the "non-polar" interactions represented by **dispersion or polarizability**. Electronegativity differences are often used to determine bond type. A difference in electronegativity of 0 to 0.4 indicates a nonpolar covalent bond with little to no ionic character. As atoms in a molecule approach each other through random motion their electron clouds can distort creating induced dipoles and weak attractions. Since the induced dipole results in a small degree of charge,

interactions between particles occur to minimize and stabilize any degree of charge. These have also been called dispersion interactions in the literature. Some examples:

- Aromatics are more polarizable $\delta D \sim 18$
- Chloro-aromatics are even more polarizable $\delta D \sim 19$
- Alkanes are too boring to be polarizable $\delta D \sim 14$

Permanent dipole interactions cause a second type of cohesion energy, the **polar** cohesive energy. Electronegativity differences are used to determine the degree of ionic character a covalent bond has. As a rule of thumb, differences in electronegativity between 0.5 to 1.8 display polar covalent bonds which result in a designation of δ- on the atom with the higher electronegativity value and δ+ on the atom with the lower electronegativity value. The resulting particle charges are stabilized by interactions.
Some examples:

- Alkanes, aromatics are not polar $\delta P \sim 0$
- Acetonitrile is massively polar $\delta P \sim 18$

The third major cohesive energy source is **hydrogen bonding**. The same electronegativity differences that are used to determine polar covalent are used to determine hydrogen bonding. Hydrogen bonding is the attraction of a polar δ+H, the δ+ must be on a polar H, along with an electronegative atom such as δ-O, δ-F and δ-N from neighboring molecules. The basis of this type of cohesive energy is attraction among molecules because of the hydrogen bonds.
Some examples:

- Alkanes, aromatics $\delta H \sim 0$
- Methanol > Ethanol $\delta H \sim 20$
- Acetone $\delta H \sim 5$

Calculating Solubility Using the Three Parameters
In general, solvents have precise HSP values based on their δP, δD and δH values. Solutes (the polymer in this case) have solubility that is defined by a sphere – a region of solubility with a radius Ro. It's not a single point. The HSP distance between two molecules, conventionally called Ra, is the measure of how alike the solvent and solute are. The smaller the Ra, the more likely the Ra falls within the sphere, and the more likely the solvent and solute are to be compatible. If the Ra falls outside the sphere, then solubility is unlikely. The famous formula used for nearly 50 years to **calculate the Ra** is:

$$Ra^2 = 4*(\delta D_2 - \delta D_1)^2 + (\delta P_2 - \delta P_1)^2 + (\delta H_2 - \delta H_1)^2$$

Let δD_1, δP_1, and δH_1 be dispersion, polarity and hydrogen parameters for the solvent. Then δD_2, δP_2, and δH_2 can be the values for the solute. People often ask if it matters which substance is 1 and which substance is 2. It should not because the differences in value are squared, so any negative values will cancel out.

The **radius of the sphere of the solute/polymer (Ro)** can be adjusted if one finds experimentally that the solute region of solubility is larger or smaller than expected.

Once you have the values for Ra and Ro values, you can calculate the **relative energy difference (RED).**

RED = Ra/Ro; where Ra = the HSP distance of a solvent to the center of the solute sphere and Ro = the radius of the solute sphere.

If RED>1 then the Ra value is outside the solute sphere and solubility is unlikely

If RED < 1, then the Ra value is inside the solute sphere and solubility IS likely

If RED = 1, then the Ra value is on the periphery of the solvent sphere and solubility may be possible, but it may take a while.

This is a very simple lab.
1. You will first do some pre-lab homework to calculate the compatibility of 10 solvents with polyisoprene based on their Hansen Solubility Parameters. HSP values for the solvents and the solute/polymer, and a value for Ro will be provided. From these values, you will calculate Ra and RED values for each solvent/polyisoprene combination.
2. Based on the Ra and RED values, you will predict the likelihood that each solvent will dissolve the polymer
3. Enter your calculations and predictions into the worksheet provided
4. Test each solvent on a blown-up balloon as described in Methods below and record your results.

Pre-lab homework

Step 1. Calculate the Ra value for each solvent compared to the solute/polymer. Enter the results in the worksheet. Note that the formula is set up to calculate Ra^2 so you will need to take the square root to determine the value for Ra.

Step 2. Obtain the Ro value. For the purposes of this lab, let the Ro value be 2.2.

Step 3. Calculate the RED values for each solvent.

Step 4. Predict whether or not the solvent will dissolve the solute/polymer or not. You can predict solubility with terms such as likely, unlikely, possibly.

Step 5. Begin the experimental part of this lab where you test the solvents to see how closely your predictions come to actual results.

Materials
10 Balloons per student (a few extra may be needed as spares)
10 Dropper Bottles
Paper towels
Lab hoods with good ventilation
Safety glasses
10 Solvents:
1. Water
2. Glycerol
3. Acetic acid
4. Acetone
5. Ethanol
6. Ethyl acetate
7. Dodecane
8. 1,8-Cineole (Eucalyptol)
9. d-Limonene
10. Toluene

Methods
1. Wear safety glasses
2. Blow up and tie off your 10 balloons. We suggest you use the long skinny balloons that are used to make balloon animals and tie them to make a pretzel shape. This will make them easier to work with.
3. Each fume hood should contain two or three of the solvents in dropper bottles. Toluene should be in a separate fume hood if possible or do toluene at the end, remove all other solvents and have everyone do toluene at the end.
4. Put a paper towel on the tabletop under the fume hood. Place an inflated balloon on the paper towel. Depending on the number of students in the lab you may need to take turns working in the fume hoods.
5. You can start with any one of the solvents. Using a dropper, draw up into the dropper one of the solvents. Be careful not to draw the solvent up into the dropper bulb. Drip 2-3 drops of the solvent onto the surface of the balloon. Beware! The solvents that dissolve polyisoprene (polymer) will pop the balloon with a loud BANG. This can also cause the solvent to spatter so make sure you close the fume hood about ¾ the way before you add the drops of solvent to the balloon.
6. If nothing happens after a couple of minutes, you can assume the solvent is not going to dissolve polyisoprene and enter your result into the worksheet. You can decide the scale you use to report results. One useful approach is to give a 1 for solvents that quickly dissolve the balloon, 0 for solvents that do not, and 2 for solvents that dissolve the balloon after a delay.

7. Do not reuse any of the balloons in the test of the remaining solvents. Solvents as mixtures may give misleading results.
8. Repeat this procedure for all the solvents.
9. Calculate the Ra value for each of the solvents and compare the relative score that you assigned to each of the solvents you tested. Do the values have the same pattern as your results?
10. Determine whether the score you assigned for each solvent is in alignment with the calculated RED values and your predictions. If they are not the same, provide possible reasons for the deviation.

Results

Enter results into the following worksheet (also available as separate worksheet)

Chemical Name	dD	dP	dH	Ro	Ra²	Ra	RED	Prediction	Results
polyisoprene (polymer/balloon)	17.4	2.99	2.74	2.2	na	na	na	na	na
Candidate Solvents									
water	15.5	16	42.3	n/a					
glycerol	17.4	11.3	27.2	n/a					
ethanol	15.8	8.8	19.4	n/a					
acetic acid	14.5	8	13.5	n/a					
acetone	15.5	10.4	7	n/a					
ethyl acetate	15.8	5.3	7.2	n/a					
dodecane	16	0	0	n/a					
1,8-Cineole (Eucalyptol)	16.7	4.6	3.4	n/a					
d-Limonene	17.2	1.8	4.3	n/a					
Toluene	18	1.4	2	n/a					