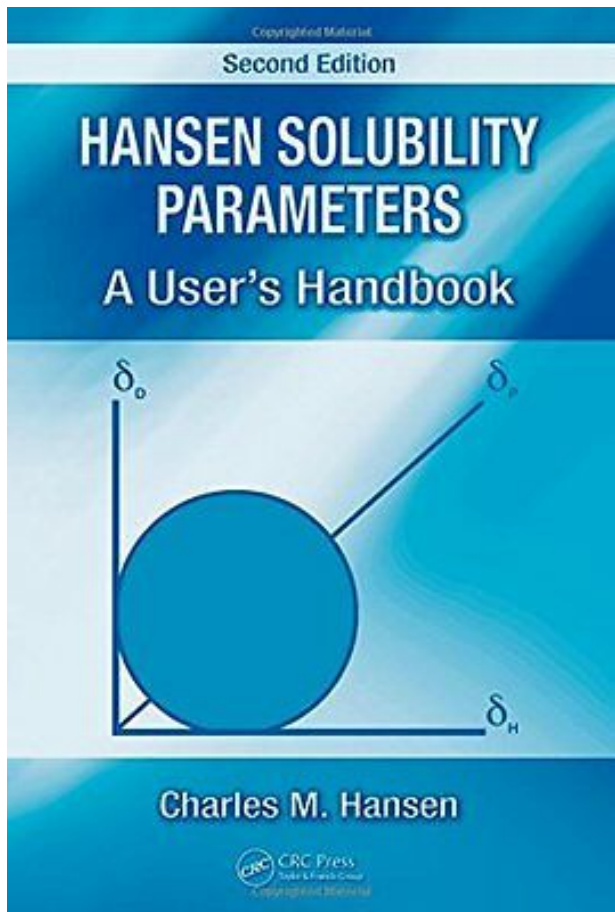




# Hansen Solubility Parameters: Theory and Application

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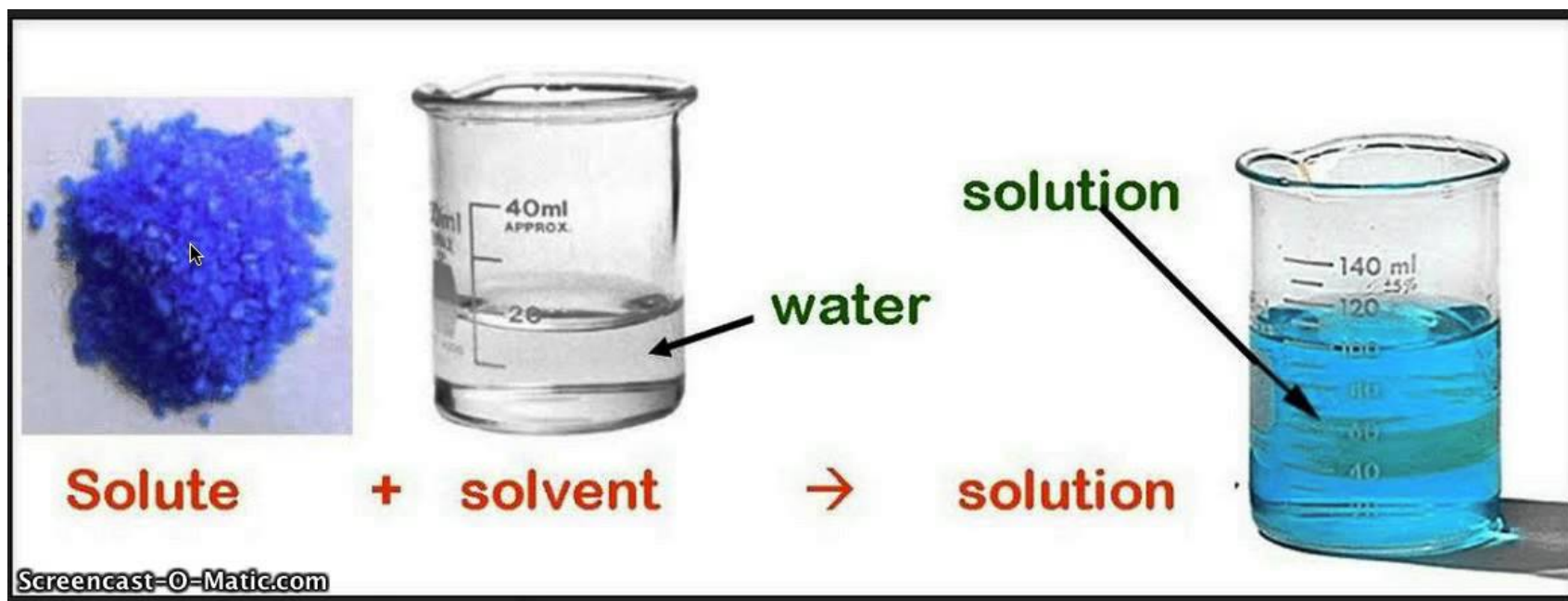


# Hansen Solubility Parameters Theory

<https://hansen-solubility.com/>

# Basics

## Solute + Solvent = Solution



- The solid solute is the substance being dissolved (e.g. a polymer)
- The liquid solvent dissolves the solute. Both substances must be similar to dissolve.
- When the solute is dissolved a solution is created.

# Solubility

- Hansen Solubility Parameters (HSP) theory is based on the relationship between energies of the solute and solvent.
- “Like Dissolves Like” is the fundamental concept.

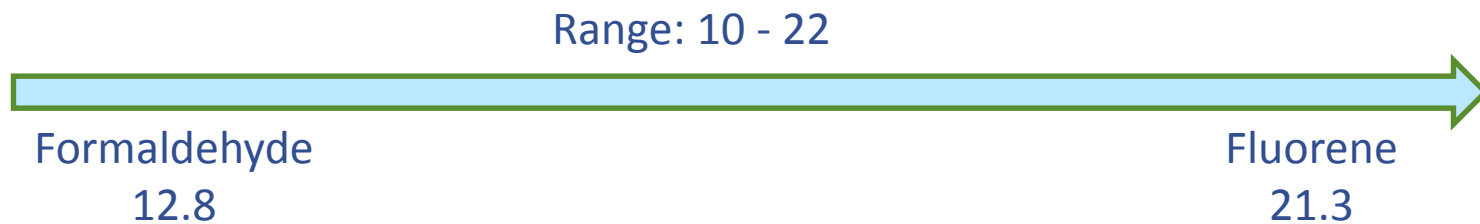
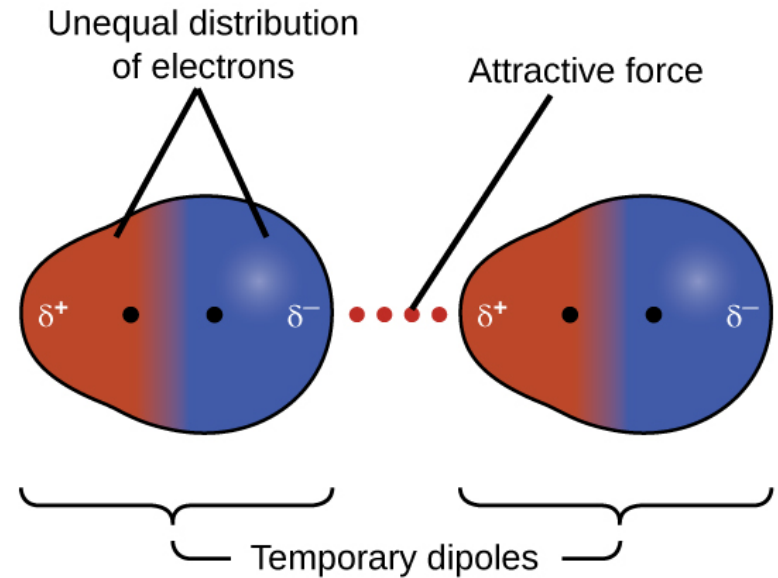
# Inter-molecular forces

1. Dispersion force (also called London Force)
2. Polar force (also called dipole-dipole force)
3. Hydrogen bonding force
4. Ionic Force (not included in HSP theory – mostly used for aqueous applications)

Strength of forces: hydrogen bonding > polar > dispersion

# Dispersion Force

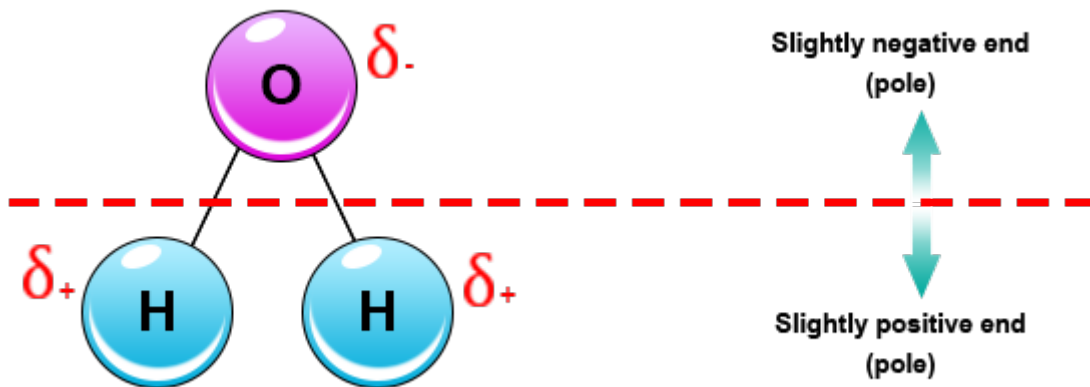
- While the electron cloud surrounding an atom is, on average, evenly distributed, at a given moment, the electron distribution may not be.
- This causes a temporary, non-localized (disperse) polarization force. This is a component of the van der Waals force.





# Polar Force

- Dipole moments occur when atoms of the same molecule have different charges.
- This causes a permanent polarization, from a specific, fixed location.
- The partially positively charged part of a molecule interacts with the partially negatively charged part of the neighboring molecule.



Non-polar

Range: 0 - 27

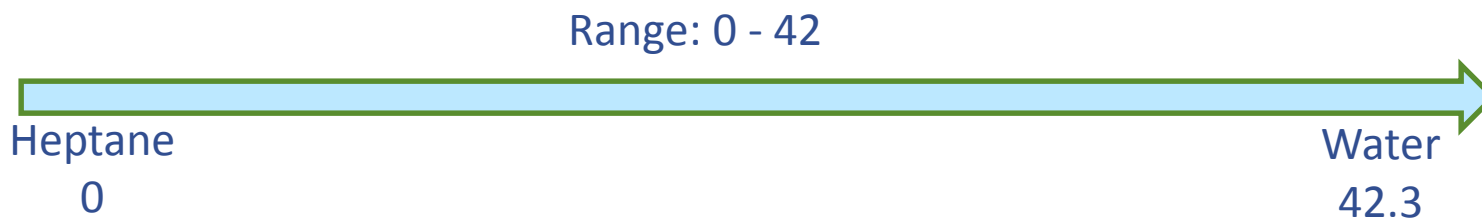
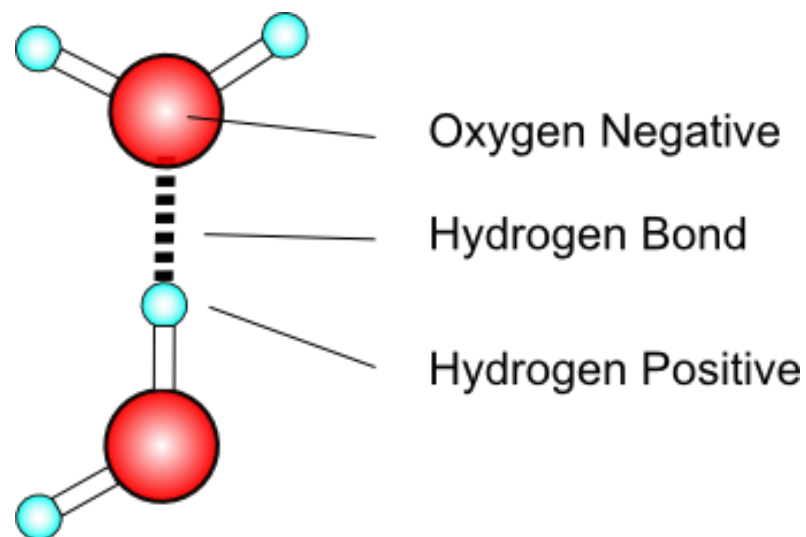
Polar

Hexane  
0

Glycerol carbonate  
25.5

# Hydrogen Bonding Force

- Occurs in molecules containing highly electronegative elements (i.e. Fluorine, Oxygen, or Nitrogen) directly bound to hydrogen.
- This force exists between hydrogen atoms and other atoms present in adjacent molecules.





# HSP Equation

- The basic equation governing the Hansen Solubility Parameters is that the total cohesion energy (molecular stickiness),  $E$ , is the sum of the individual intermolecular energies that make up the compound.

$$E = E_D + E_P + E_H$$

# Cohesive Energy Density

Larger molecules have larger cohesive energies than small molecules.

To scale the information we need to calculate the **cohesive energy density** by dividing cohesive energies by molar volume  $V$ :

$$E/V = E_D/V + E_P/V + E_H/V$$

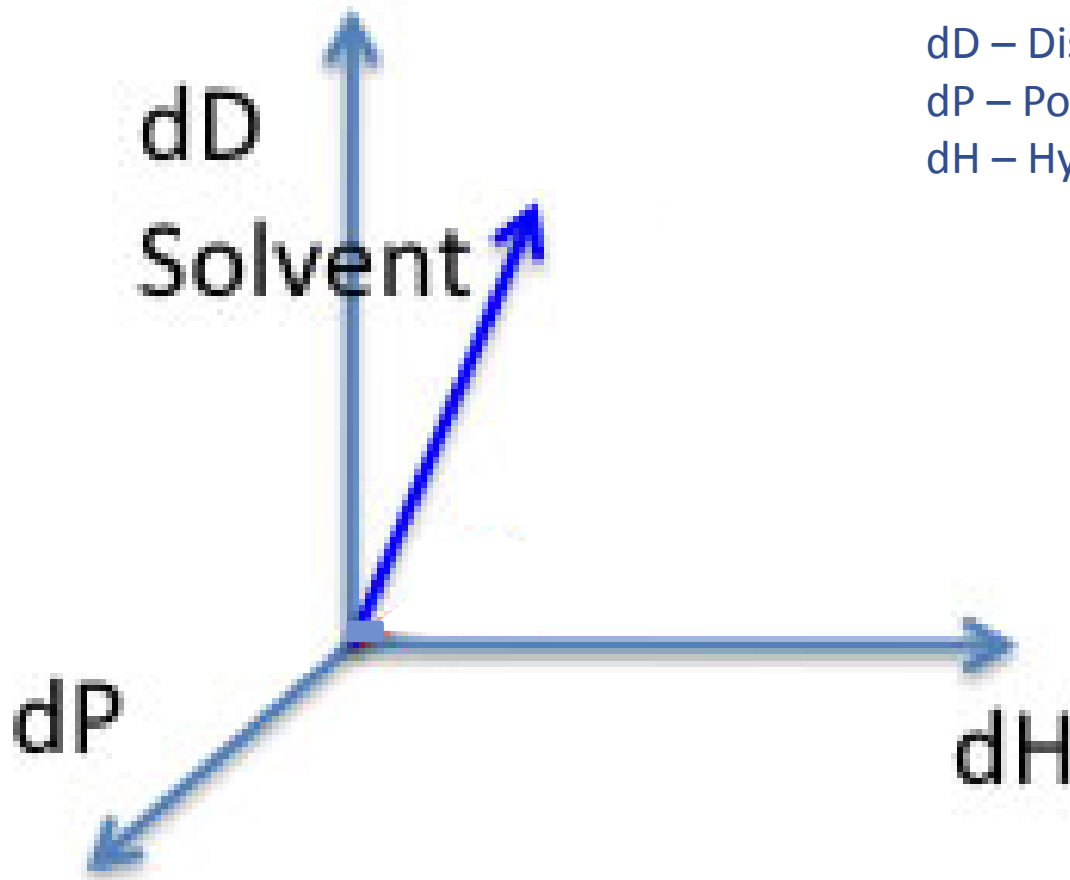
The cohesive energy density can be expressed in terms of the **solubility parameter**  $\delta$  where  $\delta^2 = E/V$ .

This gives us the formula for **Hansen Solubility Parameters** where  $\delta$  is broken into  $\delta_D$ ,  $\delta_P$  and  $\delta_H$  for Dispersion, Polar and Hydrogen-bonding:

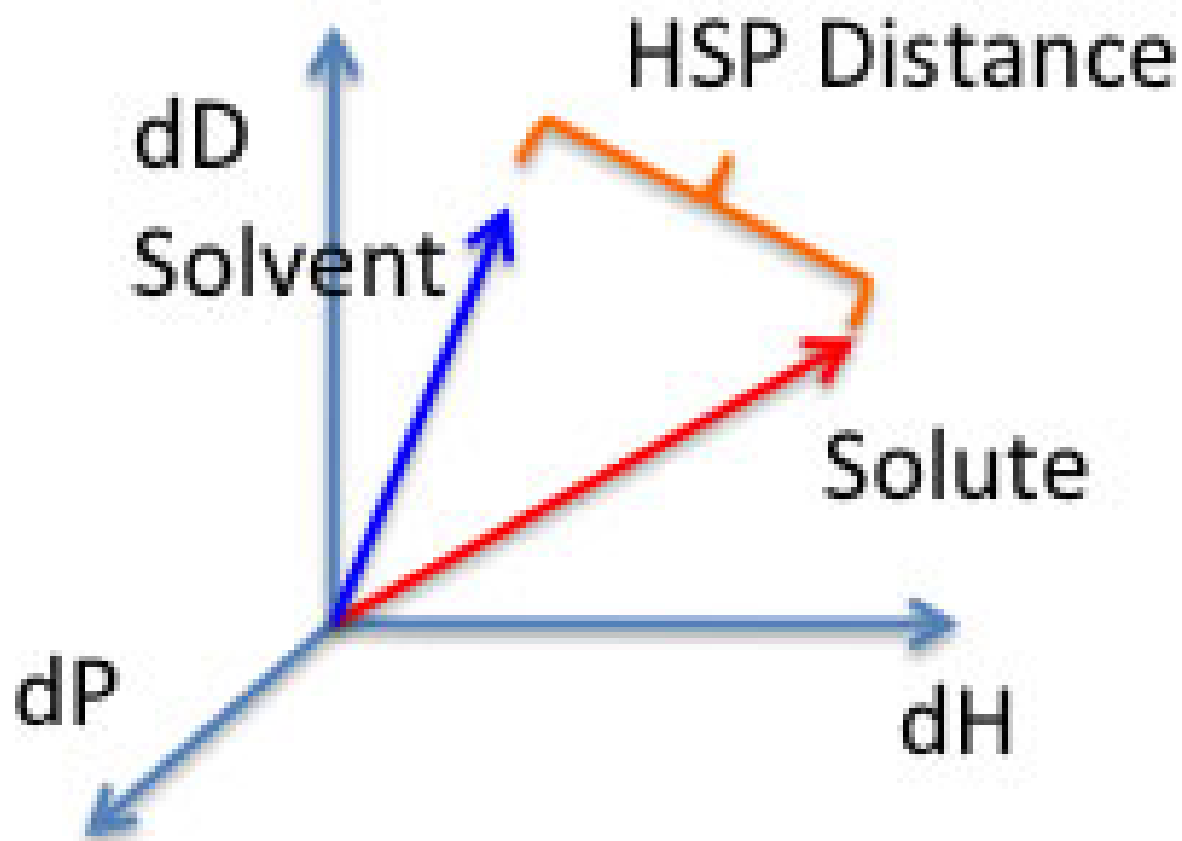
$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$

The units of solubility parameters are  $\text{MPa}^{1/2}$ . Older references use  $(\text{cal/cc})^{1/2}$  which are a factor of 2.0455 smaller.

# Cohesive Energy Density - Solvent

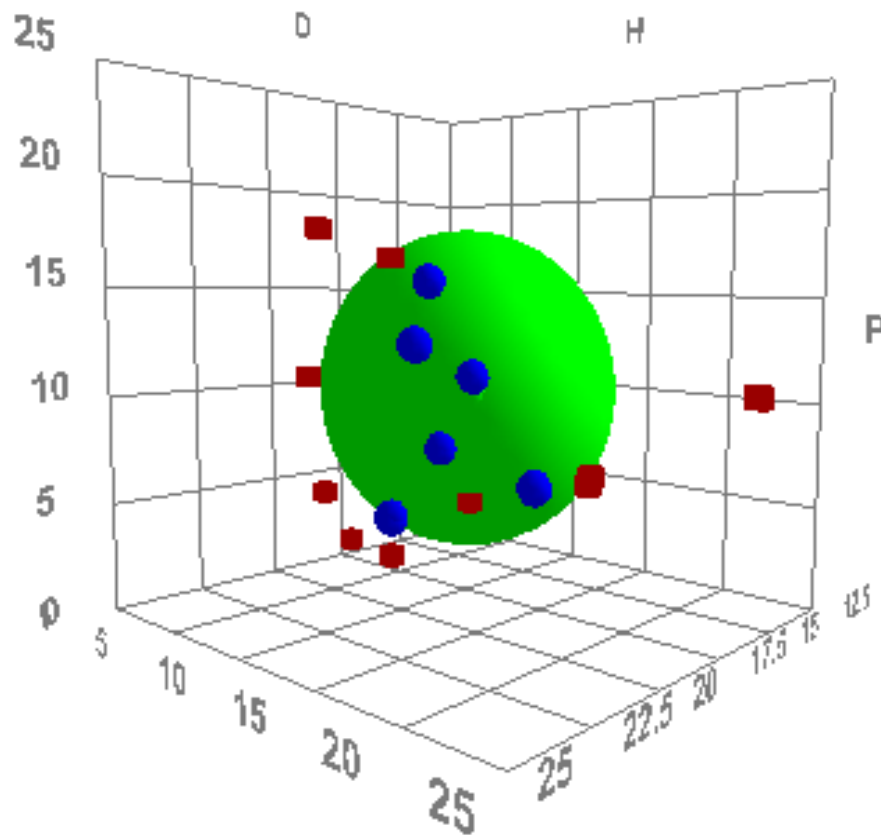


$dD$  – Dispersion parameter  
 $dP$  – Polar parameter  
 $dH$  – Hydrogen-bonding parameter



$$\text{Distance}^2 = 4 (\delta D_1 - \delta D_2)^2 + (\delta P_1 - \delta P_2)^2 + (\delta H_1 - \delta H_2)^2$$

(basically the standard distance in 3D space with a tweak for  $\delta D$ )

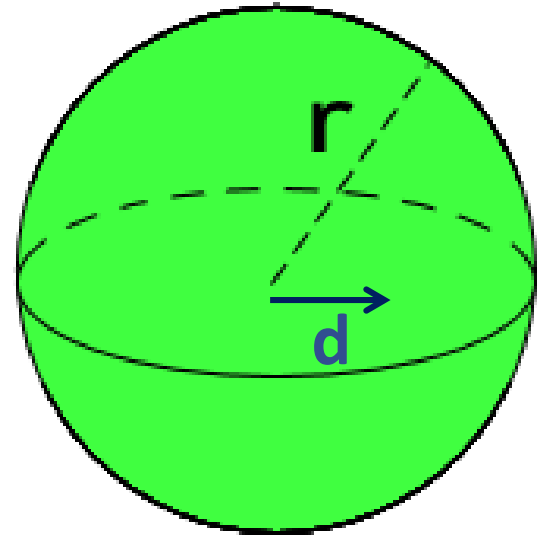


$\delta D$ ,  $\delta P$ , and  $\delta H$  are plotted in 3D space for solute and solvents.

Around the solute center point is a Green sphere of solubility, with a unique radius.

- Blue Dots: solvents that will dissolve the solute (inside or on surface of the green sphere)
- Red Cubes: solvents that will not dissolve the solute (outside of the green sphere)

## The Relative Energy Difference (RED) is calculated as:



$$\text{RED} = \frac{\text{distance of your solvent/blend to center of the solute sphere}}{\text{radius of the solute sphere}}$$

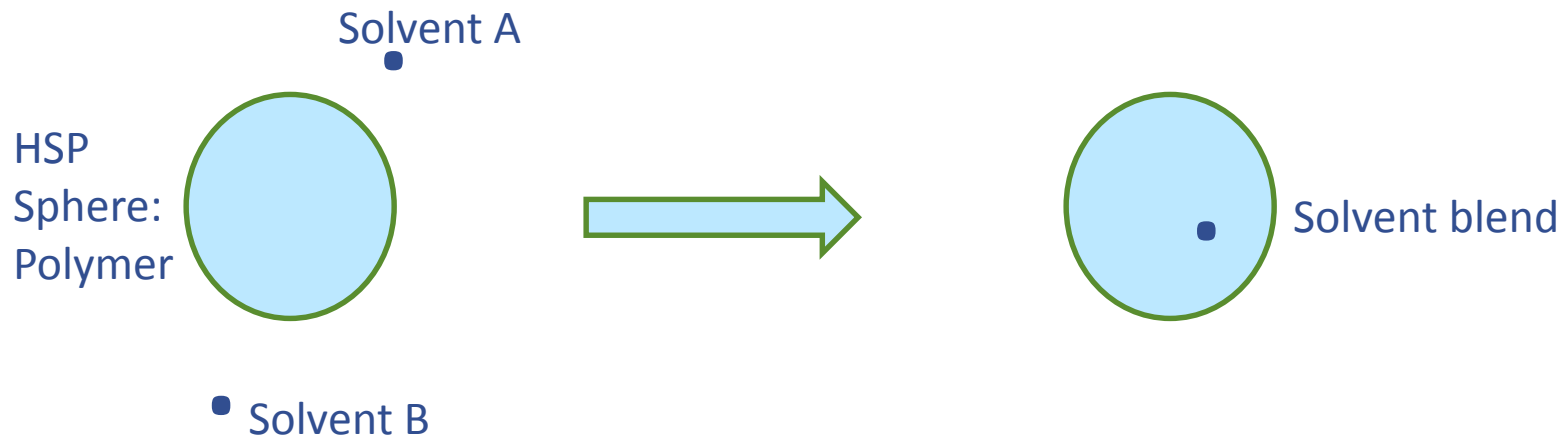
- A perfect solvent has a RED of 0.
- A solvent just on the surface of the sphere has a RED of 1.
- If  $\text{RED} > 1$  solute and solvent are incompatible,
- If  $\text{RED} < 1$  solute and solvent are compatible.

Relative RED values are useful. If Solvent A has a RED = 0.2 and Solvent B has a RED = 0.4 you know:

- a) Neither is perfect, and
- b) Solvent A is better than Solvent B

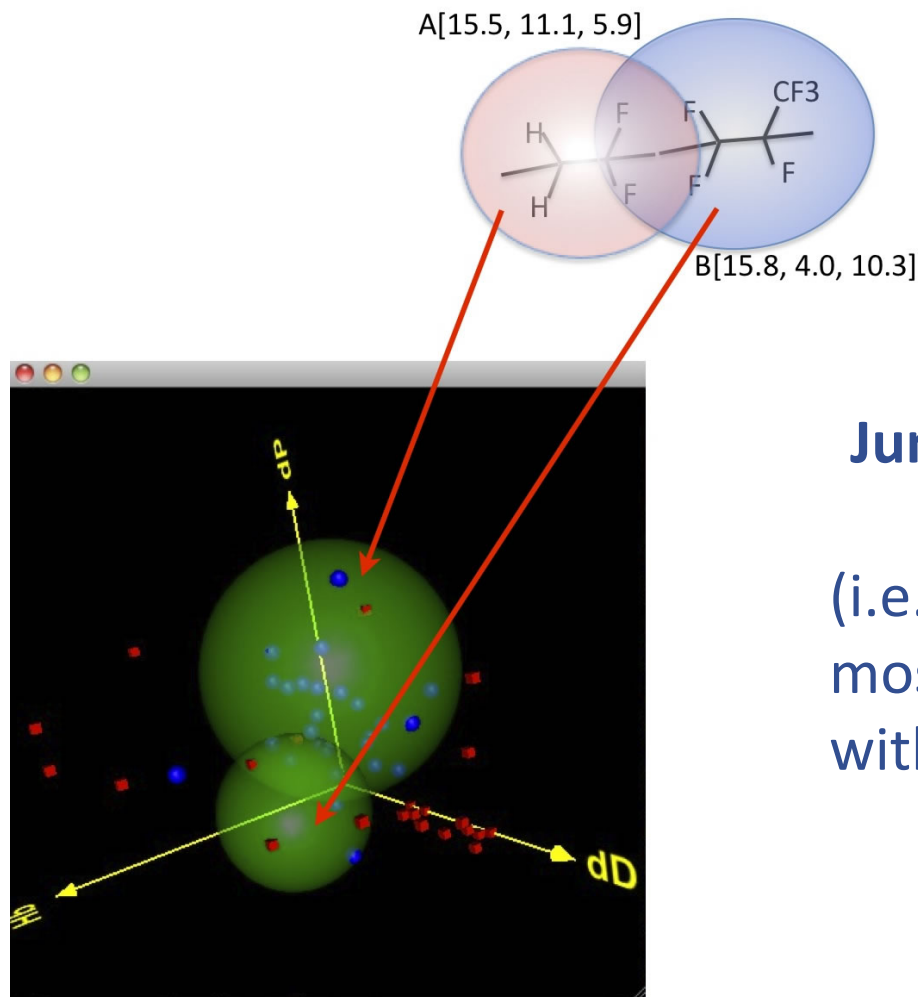
# Solvent Blends - Example

Solvent	Volume %	D	P	H
Solvent A	50%	12	4	21
Solvent B	50%	18	11	3
Solvent Blend		15	7.5	12





# Multiple Solutes

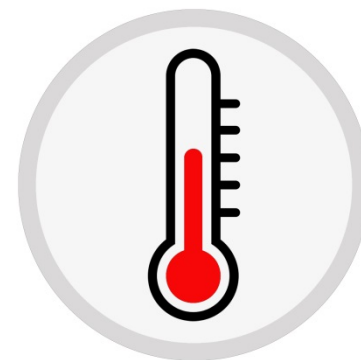
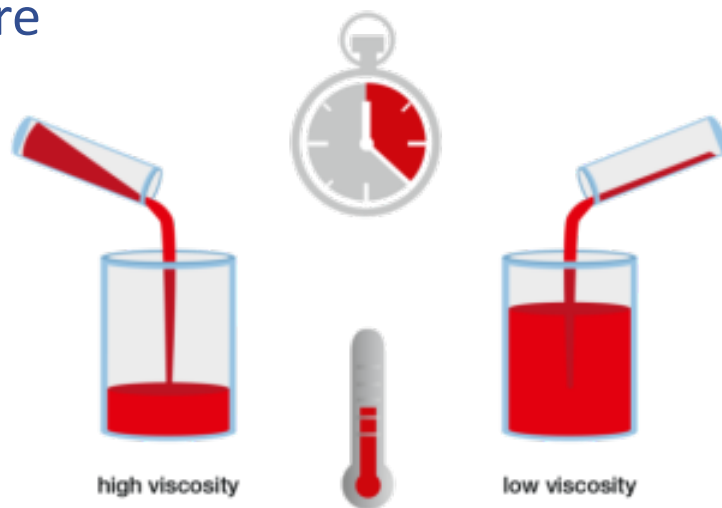


Source: <https://www.pirika.com/NewHP/PirikaE2/Sphere-Db1.html>

# Factors that Affect HSP Performance

Other than the theory based on thermodynamics, there are kinetic considerations, such as the rate of which the thermodynamic properties will be obeyed. Some of these considerations alter the HSP theory:

- Molar Volume
- Temperature
- Viscosity
- Time



# Factors that Affect HSP Performance

## Molar Volume (or Molecular Weight Effect)

- The volume occupied by one mole of a substance at a given temperature and pressure.
- Especially important when dealing with polymers.
  - The smaller the molar volume, the greater chance of solubility.
  - The larger the molecule, the slower the diffusion rate.
  - Excessively high molecular weight means that it will take far too long to dissolve it and so only swells it.

## Temperature Effect

- As temperature increases from ambient to boiling point,
  - $\delta P$  and  $\delta H$  decline slightly
  - $\delta D$  can decline by approximately 10%

# Factors that Affect HSP Performance

## Viscosity Effect

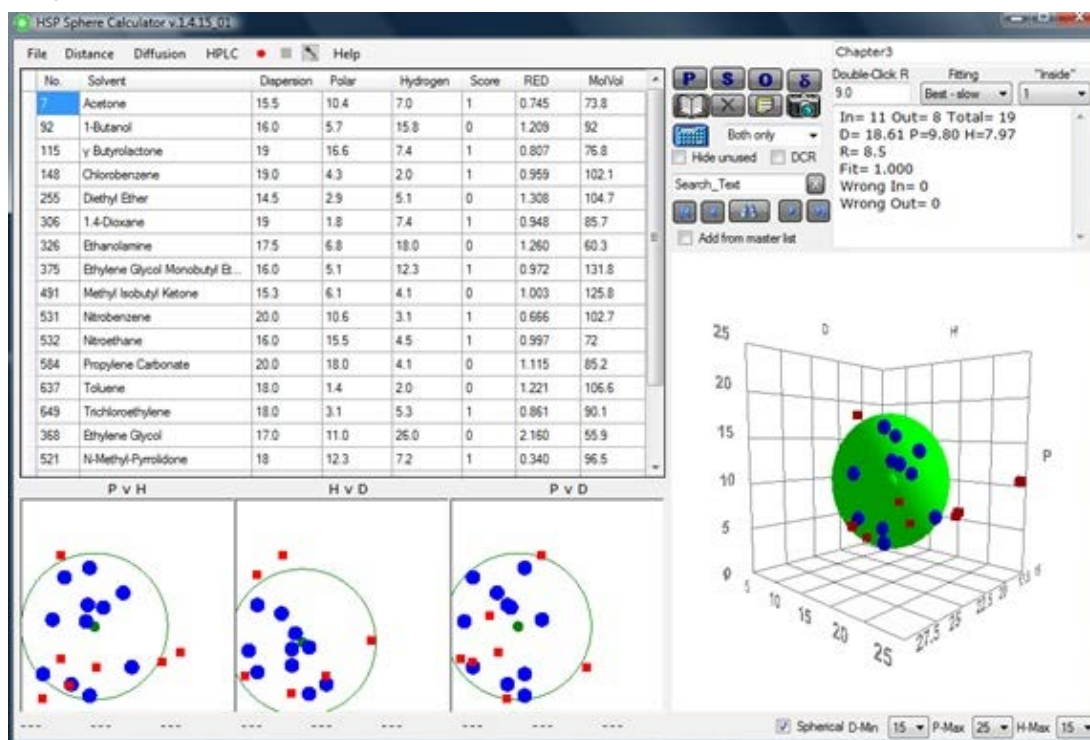
- Viscosity hinders contact between a low-viscosity fluid (such as a solvent) and high viscosity fluid (such as a heavy oil, grease, or polymer).
- It acts like a brake, reducing momentum transfer between phases, thereby reducing the ability to mix.

## Time Effect

- The rate at which equilibrium is achieved is determined by transport properties (how molecules move) which affect heat, mass, and momentum transfer.
- Transport rates can affect solubility experiments.
  - Therefore, sufficient time should be provided for the experiment to allow for diffusion to achieve complete solution/compatibility.

# Hansen Solubility Parameters in Practice

- The HSPiP program takes the theory and rapidly applies the underlying calculations.
- Provides 3D interactive graphs, solvent blend options, RED calculations, etc.



# Hansen Solubility Parameters Application

# Applications of the HSP Theory

Finding a solvent for a new polymer or chemical

Identifying appropriate personal protective equipment

Controlling flavor/aroma migration through packaging materials

Looking to cause or prevent skin permeation

Replacing a toxic solvent with a safer solvent



# Personal Protection Equipment Selection



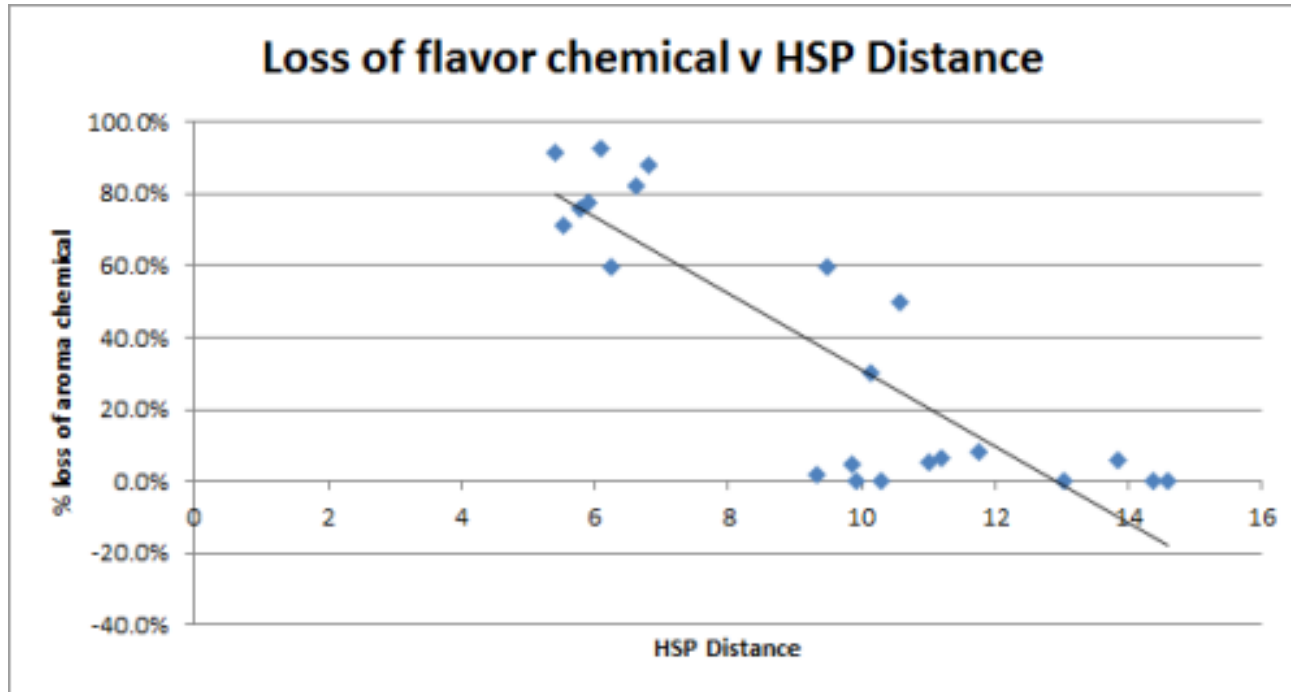
For less common solvents there may be no protective glove recommendation

- In general, the larger the HSP distance between the solvent and the glove material (solute) the better the protection provided by the glove.

Must consider other factors that can affect diffusion through a glove

- Percent crystallinity
- Molecule shape

# Flavor Migration



- Loss of flavor in food and beverage products is a function of HSP distance between the flavor molecule and the packaging material.
- Flavor migration is also impacted by diffusion, which depends on factors such as temperature and molecular shape/size.



# Skin Permeation

The HSP of skin is likely [17, 8, 8]

Will the formulation and active ingredient be sufficiently close in HSP Distance terms to be able to swell the skin surface and therefore create a high concentration gradient that drives rapid diffusion?

Diffusion within the skin also depends on the size of the molecule. Typically a doubling of the molecular weight will see the diffusion coefficient decrease by a factor of 8.

Source: <https://www.hansen-solubility.com/HSP-examples/skin.php>

# Find Safer Solvents to Replace Highly Toxic Solvents



Paint strippers with methylene chloride, NMP, toluene, methanol, xylene



Contact adhesives with toluene, hexane, xylene



Windshield washer fluid with methanol

# Hansen Solubility Parameters Project Examples

# TURI Academic Research Grants

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Every academic year TURI provides research funding to University of Massachusetts faculty and their graduate students, encouraging university and industry partnerships.

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The goal of this funding is to promote research for the identification, development, and evaluation of safer, technically feasible and commercially viable alternatives to identified toxic chemicals currently in use by Massachusetts companies.

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To date, over 100 research projects from the various UMass campuses have been supported by TURI.

# Academic Research Examples

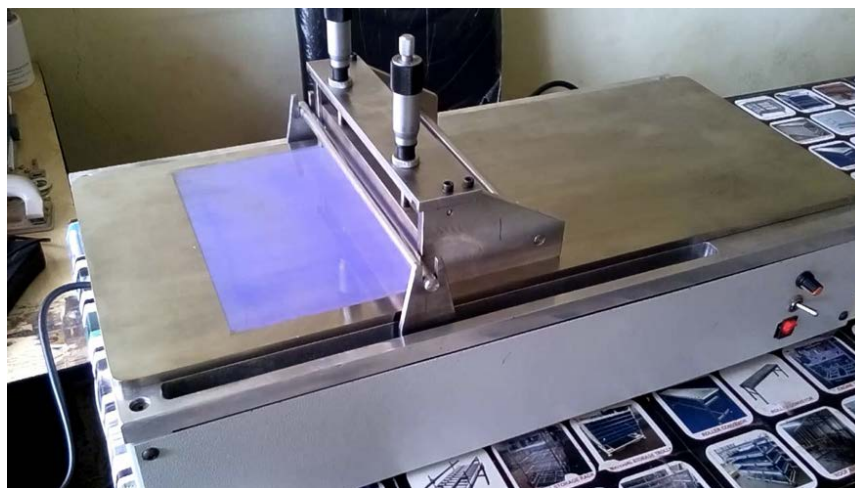
Toxic Solvent	Application	Faculty	Massachusetts Industry Partner
<b>Dimethylformamide</b>	Textile coatings	Dr. Ram Nagarajan Plastics Eng., UML	Bradford Coatings
<b>Acetonitrile</b>	Liquid chromatography	Dr. Hsi-Wu Wong Chemical Eng., UML	Waters Corporation
<b>Methanol</b>	Windshield washer fluid	Dr. Sarah Perry Chemical Eng., UMA	Camco
<b>Toluene, Hexane</b>	Contact adhesives	Dr. Chris Hansen Mech. Eng., UML	ITW Polymers



# Academic Research Examples

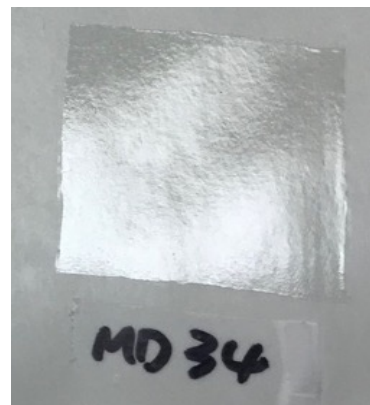
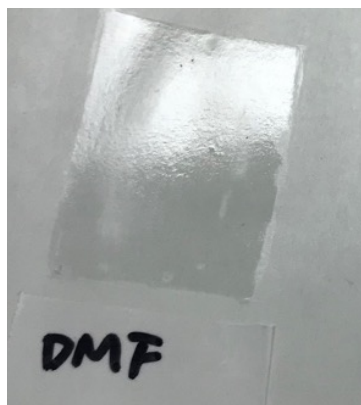
Identifying a safer alternative to dimethylformamide (DMF), a carcinogen, for textile coating applications:

- Professor Ram Nagarajan of the Department of Plastics Engineering at UMass Lowell
- Bradford Industries of Lowell



# Requirements for DMF Alternative

- Toxicity profile safer than DMF
- Dissolves the polymer (PU-polyester) up to 25% polymer loading
- Boiling point  $> 150^{\circ}\text{C}$
- Relative evaporation rate  $< 100$
- Cost  $\leq \$0.65/\text{lb}$
- Viscosity comparable to DMF solution ( $< 10,000$  cP with 25% polymer dissolved)
- Wets the substrate well
- Forms uniform coating on the substrate



# Safer Solvents for Liquid Chromatography

Identify and test the performance of safer solvent alternatives for liquid chromatography equipment

- Assistant Professor Hsi-Wu Wong of the Department of Chemical Engineering at UMass Lowell
- Waters Corporation of Milford

# Safer Solvents for Liquid Chromatography (LC)

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Liquid chromatography, such as high performance liquid chromatography (HPLC), is one of the most widely used analytical techniques in manufacturing, pharmaceutical, and legal industries to identify and quantify organic compounds.

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It requires the usage of solvents, estimated to be 34 million liters per year.<sup>[1]</sup>

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The most commonly used solvents are *methanol*, *acetonitrile*, and *tetrahydrofuran*, all of which pose significant human health concerns.

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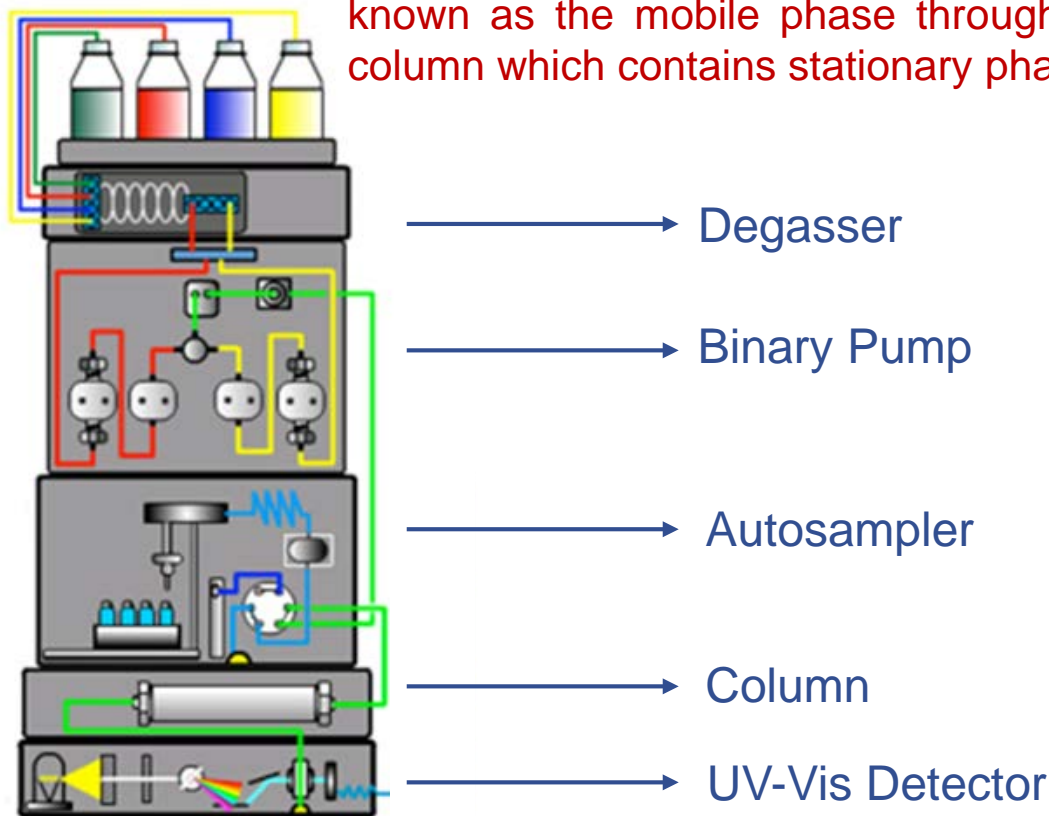
Acetonitrile is widely used in research settings for reverse phased gradient separations, is much more expensive than methanol, has several toxicity concerns (e.g. organ toxicity), and has HSP parameters that can be readily met with solvent blends.

# High Performance Liquid Chromatography (HPLC)

WATER                      SOLVENT



HPLC pumps a sample mixture or analyte in a solvent system commonly known as the mobile phase through a column which contains stationary phase



Separation of analyte happens based on the analyte's interaction with the mobile phase and stationary phase

# Operation Requirements for Selecting Green Solvents / Solvent Blends

Operation requirements for selecting green solvents or solvent blends to replace acetonitrile include:

- **Toxicity:** safer PHAROS, P2OASys and Green Screen profiles
- **Elution strength:** small HSP distance to target solvent (acetonitrile)
- **Water miscibility:** miscible with water for gradient elution
- **UV absorbance:** transparent above 250 nm
- **Boiling point:** boiling point below 100 °C
- **Viscosity:** close to target solvent/water mixture
- **Cost:** close to the cost of acetonitrile
- **Corrosiveness:** pH close to 7

# For More Information

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