A Low-Cost Path to Solvent Blend Prediction, HSP Analysis, and Cleaning Verification – Part 2

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Summary of Part 1

One can add the benefits of Hansen Solubility Parameter analysis to their operation for a minimal cost.

In many cases, existing equipment can be modified to measure
• molar volume,
• density,
• surface tension, and
• contact angle.

HSPs are tabulated in the literature

Minimal costs associated with:
• Pt:Ir ring $397 (www.vwr.com)
• Density sinker $363 (www.vwr.com)
• Tempering beaker $94 (www.finmech.com)
• DinoLite Digital microscope $185 (www.microscope.com)

HSP analysis
• HSPiP Software and e-Book $840 (www.hansen-solubility.com)
Overview of Part 2

One can add contact angle measurements for cleanliness verification to their operation for a minimal cost with modern USB-digital microscopes and free software.

Optimizing interaction spheres and blend components can be done in Excel.

Finally, one can predict the HSPs of new solvents using group contributions (Excel), and now, using Quantitative Structure Property Relationships (QSPR) and molecular modeling programs (Gaussian, Inc).

HSPs and group contribution methods are presented in:

HSP group contribution methods are most easily implemented using:
- HSPiP Software and e-Book $840 (www.hansen-solubility.com)

Suggested molecular modeling package:
- Gaussian 09w $2,500 (www.gaussian.com)
Contact Angle: Getting Started

Sessile Drop on a solid surface.

20 µL water on Teflon

120°

20 µL acetophenone on Teflon

90°
Contact Angle and Surface Tension
Sessile Drop on a solid surface.

\[ \gamma_{13} = \gamma_{12} + \gamma_{23} \cos \theta_c \]

\[ \cos \theta_c = \frac{\gamma_{13} - \gamma_{12}}{\gamma_{23}} \]

Work of adhesion to the surface per m²

\[ w_{ad} = \gamma_{13} - \gamma_{12} + \gamma_{23} \]

Therefore,

\[ \cos \theta_c = \frac{w_{ad}}{\gamma_{23}} - 1 \]
Contact Angle: Most Inexpensive Setup
Contact Angle: Moderately Inexpensive Setup

- sample rotation
- vertical adj.
- focus
- zoom
- sample xy-stage $264 (www.microscope.com)
- zoom rail & microscope mount $633 (www.edmundoptics.com)
Contact Angle: Practical Aspects

Capture the image with a very small camera elevation.

Computer generated images illustrate why.

Measured CA = 86.8°

Measured CA = 134.6°

Measured CA = 140.8°

Measured CA = 40.8°
Contact Angle: Errors Due to Elevation

Actual CA = 40°

117% error

±5° very conservative
Contact Angle: Free Software

ImageJ is a Java-based image processing software package. Download and install the package, then download and install the Contact Angle Plugin by Brugnara.

We are evaluating the performance of the other two ImageJ plugins for contact angle (Dropsnake and LBADSA), but currently favor Brugnara’s package.
Contact Angle: Software Details

1. Load the image in ImageJ (image should be “upside down”) and run the Plugin.
Contact Angle: Software Details

1. Select five points that define the drop shape, then click analyze.

Tips:
1. Define the tri-phase points first. (follow the order shown).
2. Select the “manual points procedure”.
3. The ellipse is most reliable.
Contact Angle: Cleaning Verification

Dionized water is used as a probe of surface cleanliness. Water is attracted to the metal oxide surface layer and expresses a small contact angle. Hydrophobic contamination repels the water which expresses a large contact angle.

Deionized water on an Al 2024 surface, CA = 43°
Contact Angle: Cleaning Verification

Dionized water is used as a probe of surface cleanliness. Water is attracted to the metal oxide surface layer and expresses a small contact angle. Hydrophobic contamination repels the water which expresses a large contact angle.

Initial Al 2024 surface CA = 43°

Gross contamination, (high vacuum grease) CA = 116°

Ultrasonicated in degreaser, CA = 45°

Dry-wiped with a Kimwipe, (high vacuum grease) CA = 77°

This surface "looked very clean".
Contact Angle: Targeted Cleaning
The HSPs of the soil are needed for targeted approach.
Part 1 discussed various methods of HSP determination.

What do you do if you have a new solvent with no known HSPs?
Targeted Cleaning with New Solvents

What do you do if you have a new solvent with no known HSPs?

Group Contributions

- Can be done by hand or in Excel. However, I recommend buying HSPiP (www.hansen-solubility.com) because creating the spreadsheet will take more time ($) than the cost of the software.

Quantitative Structure Property Relationships (QSPR) being developed at SHSU.
How to Determine the HSPs for New Solvents?

Group contribution tables allow HSP prediction.

- HOWEVER, these tables are not optimized for highly nitrated species like energetic materials (our sponsor’s interest).
- These tables can be difficult to use when there are multiple ways to construct the target molecule.

Quantitative Structure Property Relationship (QSPR)

- Any structural item can be explored for correlation.
- Electronic structure calculations will provide the Quantitative Structure variables.
- Molar volume and HSPs are the Properties of interest.
- A stepwise regression is used to generate a matrix of coefficients which Relates structure and activity.
How to Determine the HSPs for New Solvents?

\[
\begin{bmatrix}
1 & S_1 & S_2 & \ldots & S_u \\
C_{0,\delta_D} & C_{0,\delta_P} & C_{0,\delta_H} \\
C_{1,\delta_D} & C_{1,\delta_P} & C_{1,\delta_H} \\
\vdots & \vdots & \vdots \\
C_{u,\delta_D} & C_{u,\delta_P} & C_{u,\delta_H}
\end{bmatrix}
= \begin{bmatrix}
\delta_D \\
\delta_P \\
\delta_H
\end{bmatrix}
\]

- Gaussian calculation output is the QSPR input matrix.
- The QSPR matrix comes from a stepwise linear regression against the training set HSPs.
- QSPR output should match the training set HSP matrix.
QSPR Results against Literature HSPs

The correlation is not perfect, but it already out-performs the group contribution methods, and is improving.

- Calculated D, P, or H / MPa^{1/2} vs. Literature D, P, or H / MPa^{1/2}

- Linear (D): $R^2 = 0.5806$
- Linear (P): $R^2 = 0.7381$
- Linear (H): $R^2 = 0.8771$
How to Use the SHSU QSPR to Determine the HSPs for New Solvents?
1. Obtain the latest QSPR matrix spreadsheet from SHSU (williams@shsu.edu).
2. Optimize the geometry of the solvent molecule in Gaussian.
   1. #B3LYP/6-31G(d) opt freq=raman
3. Extract the structural parameters from the Gaussian output file (guided by Excel).
4. Use the matrix array formula in Excel to calculate the HSPs for your solvent.

This QSPR method has several advantages:
- Based on the actual 3D structure of the solvent, not just chemical groups.
- Unambiguous procedure.
- Easily updated or tailored to specific chemistries (like explosives).
Experimental Determination of the HSPs of a New Solvent
Revisiting the original method for determining the many HSPs present in the literature:
1. Gather 15-20 polymers covering a large range of HSP-space.
2. Expose the unknown solvent to all of the polymer samples in individual vials.
3. Score the interactions and determine the center of the interaction sphere.

Advantages
• Experimental
• Dual determination of chemical compatibility of solvent and various polymers
• Simple

HSP determination of a solid or semi-solid soil.
Summary
Part 1 – Experimental determination of Solvent Properties
• Surface tension, hydrostatic density, molar volume, Hansen solubility parameters
• Basic cost estimates of in-house-added capabilities
Part 2 – Contact angle and HSP predictions
• Experimental determination of contact angle
• Cleanliness verification
• HSP predictions using HSPiP
• HSP predictions using QSPR

Questions
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