

**Final Report:
DEVELOPMENT OF SOLUBILITY PRODUCT VISUALIZATION
TOOLS**

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ABSTRACT

Western Research Institute (WRI) has developed software for the visualization of data acquired from solubility tests. The work was performed in conjunction with AB Nynäs Petroleum, Nynäshamn, Sweden who participated as the corporate cosponsor for this Jointly Sponsored Research (JSR) task. Efforts in this project were split between software development and solubility test development. The Microsoft Windows-compatible software developed inputs up to three solubility data sets, calculates the parameters for six solid body types to fit the data, and interactively displays the results in three dimensions. Several infrared spectroscopy techniques have been examined for potential use in determining bitumen solubility in various solvents. Reflectance, time-averaged absorbance, and transmittance techniques were applied to bitumen samples in single and binary solvent systems. None of the techniques were found to have wide applicability.

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EXECUTIVE SUMMARY

Western Research Institute (WRI) has developed software for the visualization of data acquired from solubility tests. The work was performed in conjunction with AB Nynäs Petroleum, Nynäshamn, Sweden who participated as the corporate cosponsor for this Jointly Sponsored Research (JSR) task. Efforts in this project were split between software development and solubility test development.

The key activity of this project was the development and testing of visualization software for modeling the 3-dimensional solubility space resulting from applying the Hansen solubility parameter approach to petroleum residua. Data for testing the software was provided by the cosponsor. This project has resulted in the development and testing of several body types for describing soluble region of 3-D solubility space. The usefulness of the “new” body types developed will best be determined through much more experience, but those that appear useful at this time are the convex hull, rotated ellipsoid, and the minimum enclosing ellipsoid. Other body types examined, including the Hansen type, have deficiencies at least some of the time or do not seem to provide useful descriptions of the data. Users of **sp3D** are cautioned that they should visually check the reasonableness of the numerical results. The ability to make this visual check is an important attribute of **sp3D**.

The second portion of this project examined potential spectroscopy-based techniques for determining solubility. Fourier-transform infrared (FTIR) spectroscopy was applied to examining bitumen and heavy oil solubility in single and binary solvent systems. Reflectance mode FTIR techniques were quickly abandoned because of high noise levels. Time-averaged experiments in single solvents in the carbon-hydrogen (CH) stretching region were also performed. In some solvents (for example isooctane and cyclohexane), however, solvent interference in the CH-stretching region prevented accurate measurements. In other tests, bitumen was dissolved in binary solvent mixtures (toluene and isooctane, for example) and, in one mixture, activated carbon was added to determine the sensitivities of absorption and transmittance IR to particulates (insoluble material). Percent transmittance was found to decrease with increased activated carbon content in the toluene/isooctane system, a desired response. However, this technique did not work with all systems, and cannot be recommended.

INTRODUCTION

Western Research Institute (WRI) has developed an automated titrimer for the accurate, reproducible determination of Heithaus (solubility-related) parameters (Heithaus 1962) in petroleum residua (Pauli 1996). This titration apparatus and method, termed Automated Flocculation Titrimetry (AFT), has been refined and improved and is finding application in the characterization of petroleum residua during pyrolysis, oxidative aging, and upgrading (Pauli 1996; Pauli and Branthaver 1998, 1999; Schabron and Pauli 1999; Schabron et al. 2001a, 2001b, 2001c). The current work explored the possibility that the AFT, coupled with selected solvent systems, could also be used to develop multidimensional solubility parameter spaces that better characterize petroleum residua.

Understanding multidimensional techniques and their application to petroleum residua requires theoretical and historical background (Schabron et al. 2001b). The dissolution of a material in a solvent, or the mixing of two liquids to form a single phase solution, will occur if the free energy of the process is zero or negative as described by the following equation:

$$\Delta G = \Delta H - T\Delta S$$

where ΔG is the free energy of mixing, ΔH is the heat of mixing, T is the temperature, and ΔS is the change in entropy. Typically in a dissolution process, the entropy term is relatively large, and the heat of mixing determines if the mixing will occur (Burrell 1955). Hildebrand described this heat of mixing as:

$$\Delta H = V ((\Delta E_1/V_1)^{1/2} - (\Delta E_2/V_2)^{1/2})^2 \Phi_1 \Phi_2$$

where ΔH is the heat of mixing, V is total volume, ΔE_x is the molar energy of vaporization of component x , V_x is the molar volume of component x , and Φ_x is the volume fraction of component x in the solution (Hildebrand et al. 1970). The term $(\Delta E/V)^{1/2}$ is called the solubility parameter δ , and is typically given in units of $(\text{cal/cc})^{1/2}$, called the Hildebrand in the United States, and units of $\text{MPa}^{1/2}$ elsewhere (SI units, numerically 2.0455 times larger). Numerical values for the solubility parameter of a solvent can be calculated as:

$$\delta = (\Delta E/V)^{1/2}$$

from the molar energy of vaporization to the ideal gas state, ΔE , and the molar volume, V . Other means of estimating solubility parameters have been described (Hildebrand et al. 1970). For large molecules or polymeric systems, group contributions can be used to calculate if the density of the material is known or can be estimated (Small 1953).

The heat of mixing two materials is dependent on the difference between their solubility parameters squared, $(\delta_1 - \delta_2)^2$. If the solubility parameters are identical, the heat of mixing is zero and the dissolution/mixing process is driven by the entropy term $T\Delta S$ alone; mixing will occur. If the solubility parameters are not identical, the term $(\delta_1 - \delta_2)^2$ will have a net positive value which will cause the energy term ΔH to oppose the entropy term. If the entropy term is less than the energy term, mixing or dissolution will not occur.

The use of the solubility parameter is complicated by the presence of dipole and hydrogen bonding interactions. For solvents and materials with strong polarity and hydrogen bonding components, dissolution is not predictable by the single component, or dispersion solubility parameter described above. Two-component and three-component solubility parameter systems have been described (Hansen 1967, Barton 1974, Wiehe 1996). For such systems, solubility is maximized when all the various components for the solvent and material being dissolved are as similar as possible. Two- or three-dimensional maps are used to describe so-called solubility zones, areas, or spheres for such systems.

The Hansen (1967) approach assumes that there are three major influences on the solubility parameter: dispersive, polar, and hydrogen bonding. This approach defines the overall solubility parameter, δ (equivalent to the Hildebrand solubility parameter), as:

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

where the D, P, and H subscripts denote contributions from the dispersive, polar, and hydrogen-bonding forces, respectively.

In a recent study, Redelius (2000) used AFT titration results to demonstrate the need and desirability of using multidimensional solubility parameters to model petroleum residua solubility. He describes a 3-dimensional stability space expressed in terms of Hansen solubility parameters. By monitoring changes in this space, his model allows prediction of residuum stability and the calculation of its sensitivity to different processes. Examples of these processes are aging, oxidation, visbreaking, and fluxing or blending residua.

The proposed work was to create and test visualization software that allows rapid, interactive exploration of the Hansen 3-dimensional stability space and to perform solubility testing to better define the solubility surface shape and location. The modeling of solubility stability during blending of petroleum residua and the selection of additives that promote stability are of particular importance.

This work involved activities in two areas. The first area of activity involved the software development and testing using the MATLAB® programming environment. The second area of activity was solubility testing to better “clarify” solubility results for marginal systems.

The goals of the software phase were to develop software to define and display an optimized body (probably not spherical) in 3D Hansen space based on:

- Hansen solubility parameters of good solvents for a residuum being inside the body,
- Hansen solubility parameters of non- or poor solvents being outside the body, and
- Hansen solubility parameters of titration precipitation points being on the surface of the body.

The software would create a 3-D plot of the result, showing the optimized body and allowing free rotation and tilting of the axes for better viewing. Simultaneous viewing of more than one body/data set would be possible. One of the body fits would be equivalent to the Hansen method. Numbers of outliers and the Hansen fit quality number would be calculated. The software would be Microsoft Windows[®] compatible and require no license or fee for distribution. AB Nynäs Petroleum would provide data sets for testing the software. Other test data would come from part two of the project.

The goal of the second part of this project was to perform AFT titrations on selected solvent-precipitant pairs and a residuum sample in consultation with AB Nynäs Petroleum. After consulting with AB Nynäs Petroleum, this goal was modified to become an investigation of solubility measurement accuracy in borderline systems. WRI and Nynäs selected infrared analysis as the principle tool for doing this.

Procedures that detect the extent to which sample dissolution has taken place are rigorously performed by mixing a sample of the test material into a large number of different solvents and recording the results based on visual observation. Clearly, more sophisticated methods, preferably instrumental (spectroscopic or light scattering) methods, are warranted to more accurately measure the degree to which dissolution/non-dissolution occurs in a given bitumen-solvent solution set.

One method that might be used to detect whether or not a sample material has completely dissolved, in a number of different solvents, is the measurement of the change in absorption by spectroscopic methods as a function of the solvents used to prepare a given sample. For example, changes in absorption in the CH-stretching IR frequency band that relate directly to changes in concentration of hydrocarbons might be monitored as a function of the dissolution solvent to detect soluble versus insoluble mixtures.

EXPERIMENTAL

Software Design

The graphical and numerical nature of this software development, coupled with the need for a stand-alone final software product, led WRI to choose the MATLAB® programming environment for writing the program. MATLAB® provides a large number of numerical analysis and 3-dimensional plotting functions. MATLAB® also supports the writing of graphical user interfaces (GUIs) for the Windows® operating system. This allows clients to run the software in a familiar, menu-and-mouse-driven, graphical setting. In addition, MATLAB® offers an optional compiler that (with some exceptions) converts the MATLAB® code to C or C++ that can then be compiled to a stand-alone software package using a C or C++ compiler. The MATLAB® environment supports advanced debugging features to aid software development.

The structure of the final software was determined in large part by the GUI-based need to be primarily mouse-driven. The software had to operate in an intuitive fashion for someone experienced in using other Windows-based programs. The structure chosen for the software has two main menus and a user support and program information menu. The first menu contains the data file manipulation tools, the program preferences, and the program exit feature. The second menu contains the data display, calculation, and report features. All of the menus and many other software features are discussed in detail, with examples, in the **sp3D** user manual located in the Appendix of this document. The final software code has approximately 3,500 lines of original code plus a large, but uncounted, number of lines in the many MATLAB® routines called from the original code. The program is currently named **sp3D** and is in its second major revision.

The solid body types that have been included in this version of **sp3D** were selected for their potential as visualization tools. At present, six surfaces types are fit to the data. They are listed below in separate sections.

Convex hull

This is the surface one would see if the set of “soluble” points was wrapped with a flexible membrane. It is the smallest convex region that contains the “soluble” data set. The fit is obtained through the MATLAB® implementation of the Qhull algorithm (National Science and Technology Research Center for Computation and Visualization of Geometric Structures (The Geometry Center), University of Minnesota 1993). The convex hull shows the smallest body containing the “soluble” points and is useful for examining overlapping data sets.

Hansen-type ellipsoid

The second surface generated by the program is a modified “sphere” as is used in the well-known Hansen fit. This is actually the ellipsoidal body described by equation 1 (Hansen

2000),

$$(\text{Radius})^2 = 4(\delta_D - \delta_{D0})^2 + (\delta_P - \delta_{P0})^2 + (\delta_H - \delta_{H0})^2 \quad (1)$$

where

Radius is the apparent body radius in solubility parameter units,
 δ_D and δ_{D0} are the data and body center coordinates along the dispersive axis,
 δ_P and δ_{P0} are the data and body center coordinates along the polar axis,
 δ_H and δ_{H0} are the data and body center coordinates along the hydrogen-bonding axis.

The variable parameters are δ_{D0} , δ_{P0} , δ_{H0} , and Radius. A goal-achieving algorithm (MATLAB® function: fgoalattain) is used to maximize the fit parameter. This quality of fit is determined identically to that described by Hansen (2000), however, the fitting algorithm is different. The coordinates of the center of mass of the convex hull are used as initial parameter values.

Axis-aligned ellipsoid

The third surface fit to the data is simply the Hansen fit described above, but with variable coefficients on the difference terms (equation 2)

$$(\text{Radius})^2 = a(\delta_D - \delta_{D0})^2 + b(\delta_P - \delta_{P0})^2 + c(\delta_H - \delta_{H0})^2 \quad (2)$$

where

a, b, and c are the new variable parameters.

All other parameters are identical to the Hansen-type fit. This is an ellipsoid with principal axes aligned in the δ_D , δ_P , and δ_H directions. A fit is performed using the center and dimensions of the minimum sized axis-aligned box for initial guesses. The Hansen fit parameter is maximized using the goal achieving routine discussed above.

Rotated ellipsoid

The fourth surface fit to the data is similar to the axis-aligned ellipsoid described above, but allows the body to rotate and tilt to obtain a better fit. This procedure adds several parameters to the fitting process, but should (and usually) results in a better overall fit. Center and dimension initial guesses are determined as in the axis-aligned ellipsoid fit. Rotation initial guesses are set to zero. The quality of fit is still determined as in the Hansen procedure and the goal achieving function is used. The fitting procedure and complex surface type sometimes lead to good, but not optimum, results for the rotated ellipsoid.

Rotated ellipsoid with convex hull center and volume

The fifth surface has the same center coordinates and volume as the convex hull, but attempts to align with the “soluble” data points to minimize distances to its surface. This is an approximation of a circumscribed ellipsoid. A least squares minimization is used to orient the

body.

Minimum enclosing ellipsoid

The sixth surface fit is the minimum enclosing ellipsoid for the “soluble” data set. It approximates the smallest volume ellipsoid containing all the “soluble” points. This is not a robust solution to the minimum-volume-ellipsoid problem, but is instead an approximation using least squares minimization. Initial guesses are based on the center and dimensions of the minimum enclosing box.

Solubility Testing

In support of ongoing work involving the development of solubility-space modeling software that is applicable to dissolution properties of heavy crude oil/bitumen in various organic solvents, Fourier-transform-infrared (FTIR) spectrophotometry has been utilized to develop a test method that measures the extent of dissolution/nondissolution of bitumen in solvent(s) for a given solution system. Reflectance, transmittance and absorption modes were surveyed in different sets of experiments. Reflectance mode infrared (IR) spectroscopy with microscopy capabilities was considered in order to detect particulates. This approach was found to result in very scattered data and was quickly abandoned. The other two IR-modes were more thoroughly explored. A summary of tests and conditions is shown in Table 4.

Bitumen dissolution in four organic solvents at three concentrations

Bitumen’s AAD-1, AAG-1 and AAM-1 were prepared in solutions of toluene, isooctane, cyclohexane, and carbon disulfide at 0.1%, 1.0%, and 10% concentration levels (expressed in weight of bitumen to volume of solvent). Prior to analysis by FTIR, solutions were shaken or swirled to promote sample dissolution in a timely manner. For solutions prepared in either carbon disulfide or toluene, only a few hours of dissolution were required. In contrast, solutions prepared in either cyclohexane or isooctane were left overnight, where solutions prepared with isooctane were periodically stirred, and in some cases placed in a water bath at 104°F to 122°F (40-50°C) for periods of 2 hours and 3 hours. For cyclohexane solutions that were also left overnight, no further method of preparation was required. However, based on visual observation of the sides of the vial at the two higher concentrations, asphaltic residue was occasionally observed in some samples. Furthermore, it was apparent, based on visual observation, that samples prepared in isooctane were never completely dissolved, especially at the higher concentrations where asphaltic residue was observed to adhere on the sides of the vial each time.

IR-spectra were collected for each of the solutions described above, employing a Perkin-Elmer Spectrum One FTIR spectrophotometer operated in absorbance mode, to detect changes in absorption through a 0.05 mm path length KBr cell. The background spectra collected for each

sample was from the solvent used to prepare the sample. For each of the bitumen-solvent solutions prepared in each of the four solvents, a series of scans were taken over time at 5-minute intervals and compared based on integrated absorption peak-area to derive a time-averaged spectrum of the sample.

Bitumen dissolution in binary solvent solutions (Heithaus-like solutions)

In a second set of studies, bitumen-organic solvent solutions were prepared at three concentration levels (0.09 g/mL, 0.116 g/mL, and 0.5 g/mL), such that the total volume of solvent, V_1+V_2 , was comprised of a binary mixture of solvents, 1-isooctane and 2-toluene. Three binary mixtures of solvents were prepared at volume fraction levels of 0% (bitumen in toluene w/ no isooctane), and at 25% isooctane:toluene, 50% isooctane:toluene, and 75%(v/v) isooctane:toluene, respectively. IR-spectra were collected for each solution where the background spectra corresponded to the specific binary solvent concentration levels used to prepare the sample. For samples prepared at 0.116 g/mL and 0.5 g/mL, no further analyses were conducted. For 0.09 g/mL solutions, a 5% by weight amount of activated carbon (AC) (weight of AC per weight of bitumen initially present in the sample) was added, stirred for a few minutes, and immediately scanned a second time by IR to measure the change in absorption and transmittance resulting from the addition of the AC.

RESULTS AND DISCUSSION

Software Testing

Several solubility data sets were examined using **sp3D**. These included seven provided by Nynäs, one taken from Hansen (2000), and two artificially created through modifications of one of the Nynäs-supplied data sets. The results from analyses of these data sets are organized in three groups shown in Tables 1 through 3.

Table 1 shows the sensitivity of the body centers, outliers, and fit qualities to translation of the data set along the polarity and hydrogen-bonding axes. The original data set, **b1**, was modified by adding 4 solubility units to all polar coordinates to make data set **b2**, and by adding 4 solubility units to all hydrogen bonding coordinates to make data set **b3**. For these data sets, the effects of shifting data sets appear small. The only body location parameters that do not shift 4 units are those for the minimum enclosing ellipsoid where the fit shifts are 3.9 and 3.8 for **b2** and **b3**. Fit qualities are unchanged, except for the minimum enclosing ellipsoid. The best fits for the data sets are provided by the axis-aligned ellipsoid, followed by the rotated ellipsoids. In principle, the rotated ellipsoids should always provide at least as good a fit as the axis-aligned ellipsoids. In practice, it has been difficult to develop an algorithm for selecting initial orientation guesses that ensures the best out of many good fits. The values of the Hansen fit

parameters for the ellipsoid with convex hull center and volume and the minimum enclosing ellipsoid are not expected to be high, since neither fit type attempts to balance soluble and insoluble points. These two bodies are fit using a least squares minimization procedure. The reason for the differences in fit parameter values for the three fits using the minimum enclosing ellipsoid is not known. However, the fit parameter is not used by the fitting algorithm for this body; it is calculated after fitting is completed.

Nynäs provided two data sets in which “exact” solubility body boundaries were determined using titration with three solvents. Table 2 lists the results for fits performed with and without the “exact” points. Convex hull, Hansen-type, and rotated ellipsoid fits for bitumen AAG-1 with and without “exact” points are shown in Figures 1 through 3. The convex hull bodies show a slight shift when exact points are included because two of the exact points extend the convex hull. The other exact point (2-butanone; 16.6, 4.1, 6.6) lies within the convex hull and thus, is not a vertex. Hansen-type bodies do not have enough parameter degrees of freedom to guarantee reasonable fits. This problem is evidenced in Table 2 by the zero values for the hydrogen bonding coordinates and in Figure 2 by a flattened body shape. Having the boundary pass through the “exact” points and having limited flexibility in the shape equation lead to an unreasonable fit. A better fit, but more unreasonable result, could have been obtained by allowing the hydrogen-bonding coordinate to go negative. This is not allowed in the program. Other body types with more parameters do not have this problem. For example, Figure 3 shows an elongated, but not unreasonable, body for the data with the exact points.

Table 3 contains fitting results for three materials: two bitumen samples, **b4** and **b5**, and a lignin (data set from Hansen (2000)). Both bitumen data sets produce fits similar to those of bitumen’s **b1** (Table 1), AAG-1 (Table 2), and AAM-1 (Table 2). In four out of five cases the rotated ellipsoid provides the best fits. In all cases the Hansen-type fit used by **sp3D** provides equivalent or better-fit qualities than the reference. Interestingly, the actual best-fit coordinates are sometimes quite different between **sp3D** and the reference. This is most noticeably true for **b4** where the **sp3D** Hansen-type body fit parameter is substantially higher and the body has only 5 outliers compared to 10 for the reference fit. Another example of differences in behavior can be seen with the lignin data set. The fit qualities for the reference and **sp3D** Hansen-type fits are higher than for any other material examined. The expectation is that the resulting bodies will be good fits to the data. Figures 4 and 5 show the Hansen-type body for the lignin data set compared with the convex hull of the soluble points and with the rotated ellipsoid fit. It is obvious from viewing these figures that neither the Hansen-type nor the similar reference (Sphere) fits adequately describe the solubility of lignin. Both types of fit give misleading coordinates for the center of the soluble point distribution. Convex hull and rotated ellipsoid bodies represent the data set much better and provide more realistic and usable results.

Some problems with **sp3D** have been observed that seem to be related to deficiencies in

the MATLAB® compiler. Most of these problems appear to be computer or operating-system dependent and are manifested as graphical inconsistencies. These include figure resets that are specifically included in the original MATLAB®-based code, but inoperable in some installed versions of **sp3D**. Fill shading and opacity are sometimes inconsistent between some computers or operating systems. With a limited number of computers and operating systems available for testing, it is difficult to track and correct this type of problem. There have been MATLAB® compiler updates that might address some of these problems, but updates have not been purchased.

Solubility Testing

Three bitumen's, AAD-1, AAG-1, and AAM-1, were selected for study based on their differences in physical properties from one another. Bitumen AAD-1 is less compatible with high asphaltene content, whereas bitumen's AAG-1 and AAM-1 are both more compatible bitumen's with lower natural abundance of asphaltenes. Furthermore, bitumen AAM-1 is unusual due to its abnormally high wax content.

Figures 6 through 9 show Beer's-law plots of samples of AAD-1, AAG-1 and AAM-1, each prepared in CS₂, toluene, cyclohexane, and iso-octane at concentration levels 0.1%, 1.0%, and 10.0% (wt-asphalt/v-solvent). Clearly, Beer's law is valid for all samples prepared in solvents CS₂ and toluene for the band of the IR spectrum (CH-stretching) where integrated absorption was measured. By contrast, spectra of asphalt samples prepared in cyclohexane and iso-octane were found to be much less repeatable. It is well established in quantitative applications involving IR-spectroscopy that precautions need to be taken to select "suitable" solvents, in particular, to avoid anharmonic perturbations in peak absorption due to overlapping peaks.

In the present study, time averaged absorption values, $\langle A(t) \rangle$, defined as

$$\langle A(t) \rangle = \frac{1}{n} \sum_{i=1}^n A(t)_i$$

were determined and compared for samples containing all three asphalts prepared in both cyclohexane and iso-octane. Time-interval scan spectra were obtained by collecting spectra as a function of time at five-minute intervals; the average spectrum was then determined by summing together all time-interval scan spectra, then dividing by the number of scans.

Figures 10 through 13 show time averaged spectra derived from 5-minute time-interval scans of IR-spectra of AAG-1 prepared in four solvents, CS₂, toluene, cyclohexane, and isooctane, respectively. The samples shown here were prepared at the 10.0% (weight of bitumen/volume of solvent) concentration level. Also depicted in these four figures is 5-minute

time averaged spectra derived from time-interval scans of IR-spectra of the corresponding solvent (spectral scan of solvent with itself as the reference background). Inspection of these four figures suggests that bitumen AAG-1 prepared in CS₂ and toluene is well dissolved and free of interference of peak overlap in the CH-stretching region of the spectra as a function of time. By contrast, spectra of bitumen samples prepared in cyclohexane and isooctane are difficult to measure with much accuracy due to the overlapping peaks in the CH-stretching region of the spectra.

Both IR absorption and percent transmission (%T) spectra were also obtained for bitumen AAD-1 prepared in toluene/isooctane binary mixed solvent solutions. Figure 14 shows one of these solutions; prepared at the 0.09-g/mL (9.0% wt/v) concentration level, where a 5% (wt-AC/wt-asphalt) activated carbon (AC) was added to the solution after the initial spectra of the neat sample was previously obtained. The difference in these two sets of spectra, in terms of measuring the change in percent transmittance as a function of solutions prepared from bitumen samples containing a material such as activated carbon, compared to samples which did not contain AC, showed that %T decreased with the amount of AC added to the sample. It was anticipated that this approach could be used to detect the presence of undissolved particulates in a given bitumen-solvent sample, but this approach was not applicable to other solvents tested.

CONCLUSION

Solubility Visualization Software

The authors' experience with **sp3D** is limited to the examination of the data sets and surface types described in this report. The comments and evaluations discussed below are based on this limited experience and may change as more experience is obtained. The overall structure of **sp3D** performs fairly well, allowing flexible input of data and output of both text and graphical results and allowing flexible viewing of various surface types with or without data points. Some problems may still occur that seem to be computer or operating system dependent.

This project has resulted in the development and testing of several body types for describing the soluble region of 3-D solubility space. The usefulness of the “new” body types developed will best be determined through much more experience, but those that appear useful at this time are the convex hull, rotated ellipsoid, and the minimum enclosing ellipsoid. The other body types, including the Hansen type, have serious deficiencies at least some of the time or do not seem to provide very useful descriptions of the data.

Users of **sp3D** should be cautious with interpretations and should visually check the reasonableness of the numerical results. The ability to make this visual check is a key advantage of **sp3D**.

Solubility Testing

None of the solubility testing procedures examined in this project is applicable to a wide range of solvents and solvent blends. Signal noise and solvent interferences in the infrared region restrict the application of infrared techniques to a few solvent systems. However, some of the data acquired and modified versions of the techniques could be revisited in the future if coupled with new analysis methods.

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| Table 1. Calculated Solubility Bodies for Special Data Sets | | | | | | | | | |
|---|-----------------------------|-----------|-------|---------------------------------|------------------------|-----|-----|-----------------|-------|
| Data Set | Number of Solubility Points | | | Body Type | Body Parameter Results | | | | |
| | Soluble | Insoluble | Exact | | D | P | H | Outliers | HFIT |
| b1 | 27 | 41 | 0 | Reference (Sphere) ¹ | 19.0 | 1.8 | 3.6 | 10 | 0.841 |
| | | | | Hansen-type | 19.2 | 1.8 | 2.9 | 11 | 0.843 |
| | | | | Convex Hull | 17.6 | 4.4 | 5.1 | na ² | na |
| | | | | Axis-Aligned Ellipsoid | 18.1 | 3.2 | 5.4 | 9 | 0.894 |
| | | | | Rotated Ellipsoid | 18.0 | 4.2 | 4.2 | 9 | 0.880 |
| | | | | Ellipsoid: CHCV ³ | 17.6 | 4.4 | 5.1 | 20 | 0.739 |
| | | | | Minimum Enclosing Ellipsoid | 17.5 | 4.2 | 6.0 | 16 | 0.738 |
| b2 | 27 | 41 | 0 | Reference (Sphere) ¹ | na | na | na | na | na |
| (b1 w/ P+4) | | | | Hansen-type | 19.2 | 5.8 | 2.9 | 11 | 0.843 |
| | | | | Convex Hull | 17.6 | 8.4 | 5.1 | na | na |
| | | | | Axis-Aligned Ellipsoid | 18.1 | 7.2 | 5.4 | 9 | 0.894 |
| | | | | Rotated Ellipsoid | 18.0 | 8.2 | 4.2 | 9 | 0.880 |
| | | | | Ellipsoid: CHCV ³ | 17.6 | 8.4 | 5.1 | 20 | 0.739 |
| | | | | Minimum Enclosing Ellipsoid | 17.5 | 8.1 | 6.0 | 16 | 0.751 |
| b3 | 27 | 41 | 0 | Reference (Sphere) ¹ | na | na | na | na | na |
| (b1 w/ H+4) | | | | Hansen | 19.2 | 1.8 | 6.9 | 11 | 0.843 |
| | | | | Convex Hull | 17.6 | 4.4 | 9.1 | na | na |
| | | | | Axis-Aligned Ellipsoid | 18.1 | 3.2 | 9.4 | 8 | 0.894 |
| | | | | Rotated Ellipsoid | 18.0 | 4.2 | 8.2 | 9 | 0.880 |
| | | | | Ellipsoid: CHCV ³ | 17.6 | 4.4 | 9.1 | 20 | 0.739 |
| | | | | Minimum Enclosing Ellipsoid | 17.5 | 4.2 | 9.8 | 16 | 0.747 |
| ¹ Results from Sphere program provided by Nynäs | | | | | | | | | |
| ² Not Applicable | | | | | | | | | |
| ³ CHCV - Convex Hull Center and Volume | | | | | | | | | |

| Table 2. Calculated Solubility Bodies for Bitumens with and without Bisom Points | | | | | | | | | |
|--|-----------------------------|-----------|-------|---------------------------------|------------------------|-----|-----|-----------------|-------|
| Data Set | Number of Solubility Points | | | Body Type | Body Parameter Results | | | | |
| | Soluble | Insoluble | Exact | | D | P | H | Outliers | HFIT |
| AAG-1 | 23 | 26 | 0 | Reference (Sphere) ¹ | 18.0 | 4.4 | 3.6 | 13 | 0.753 |
| | | | | Hansen-type | 18.0 | 4.1 | 4.0 | 10 | 0.755 |
| | | | | Convex Hull | 17.6 | 4.8 | 4.4 | na ² | na |
| | | | | Axis-Aligned Ellipsoid | 17.4 | 4.2 | 4.3 | 9 | 0.851 |
| | | | | Rotated Ellipsoid | 17.7 | 4.4 | 4.5 | 9 | 0.862 |
| | | | | Ellipsoid: CHCV ³ | 17.6 | 4.8 | 4.4 | 12 | 0.730 |
| | | | | Minimum Enclosing Ellipsoid | 17.8 | 5.7 | 4.1 | 19 | 0.751 |
| AAG-1 | 23 | 26 | 3 | Reference (Sphere) ¹ | na | na | na | na | na |
| (with 3 Bisom pts) | | | | Hansen-type | 17.5 | 4.5 | 0.0 | 14 | 0.664 |
| | | | | Convex Hull | 17.5 | 4.8 | 4.3 | na | na |
| | | | | Axis-Aligned Ellipsoid | 17.7 | 4.5 | 0.8 | 13 | 0.687 |
| | | | | Rotated Ellipsoid | 17.7 | 4.8 | 4.4 | 12 | 0.822 |
| | | | | Ellipsoid: CHCV ³ | 17.5 | 4.8 | 4.3 | 12 | 0.390 |
| | | | | Minimum Enclosing Ellipsoid | 17.5 | 5.6 | 4.0 | 17 | 0.270 |
| AAM-1 | 18 | 30 | 0 | Reference (Sphere) ¹ | 18.3 | 3.5 | 2.5 | 6 | 0.831 |
| | | | | Hansen-type | 18.2 | 3.4 | 2.6 | 5 | 0.831 |
| | | | | Convex Hull | 17.7 | 5.0 | 4.3 | na | na |
| | | | | Axis-Aligned Ellipsoid | 18.6 | 4.2 | 2.8 | 6 | 0.843 |
| | | | | Rotated Ellipsoid | 18.6 | 5.8 | 4.7 | 8 | 0.849 |
| | | | | Ellipsoid: CHCV ³ | 17.7 | 5.0 | 4.3 | 15 | 0.660 |
| | | | | Minimum Enclosing Ellipsoid | 18.1 | 5.9 | 3.8 | 15 | 0.733 |
| AAM-1 | 18 | 30 | 3 | Reference (Sphere) ¹ | na | na | na | na | na |
| (with 3 Bisom pts) | | | | Hansen-type | 16.8 | 3.7 | 0.0 | 12 | 0.575 |
| | | | | Convex Hull | 17.4 | 4.5 | 3.8 | na | na |
| | | | | Axis-Aligned Ellipsoid | 18.3 | 3.0 | 1.2 | 10 | 0.700 |
| | | | | Rotated Ellipsoid | 17.9 | 4.7 | 2.7 | 12 | 0.748 |
| | | | | Ellipsoid: CHCV ³ | 17.4 | 4.5 | 3.8 | 15 | 0.322 |
| | | | | Minimum Enclosing Ellipsoid | 17.3 | 5.5 | 3.6 | 17 | 0.153 |
| ¹ Results from Sphere program provided by Nynäs | | | | | | | | | |
| ² Not Applicable | | | | | | | | | |
| ³ CHCV - Convex Hull Center and Volume | | | | | | | | | |

| Table 3. Calculated Solubility Bodies for Miscellaneous Samples | | | | | | | | | |
|---|-----------------------------|-----------|-------|---------------------------------|------------------------|------|------|-----------------|-------|
| Data Set | Number of Solubility Points | | | Body Type | Body Parameter Results | | | | |
| | Soluble | Insoluble | Exact | | D | P | H | Outliers | HFIT |
| b4 | 12 | 37 | 0 | Reference (Sphere) ¹ | 18.0 | 4.0 | 4.0 | 10 | 0.809 |
| | | | | Hansen-type | 18.3 | 2.4 | 2.7 | 5 | 0.917 |
| | | | | Convex Hull | 18.0 | 3.5 | 3.9 | na ² | na |
| | | | | Axis-Aligned Ellipsoid | 19.0 | 3.5 | 2.7 | 4 | 0.938 |
| | | | | Rotated Ellipsoid | 18.1 | 3.2 | 3.5 | 5 | 0.949 |
| | | | | Ellipsoid: CHCV ³ | 18.0 | 3.5 | 3.9 | 12 | 0.791 |
| | | | | Minimum Enclosing Ellipsoid | 17.8 | 3.3 | 3.6 | 10 | 0.884 |
| b5 | 21 | 28 | 0 | Reference (Sphere) ¹ | 18.4 | 3.8 | 3.2 | 7 | 0.899 |
| | | | | Hansen-type | 18.3 | 4.1 | 3.4 | 5 | 0.902 |
| | | | | Convex Hull | 17.8 | 5.2 | 4.4 | na | na |
| | | | | Axis-Aligned Ellipsoid | 18.1 | 3.1 | 3.8 | 4 | 0.941 |
| | | | | Rotated Ellipsoid | 18.3 | 5.1 | 4.4 | 5 | 0.946 |
| | | | | Ellipsoid: CHCV ³ | 17.8 | 5.2 | 4.4 | 14 | 0.769 |
| | | | | Minimum Enclosing Ellipsoid | 18.1 | 5.9 | 3.8 | 13 | 0.871 |
| lignin | 15 | 67 | 0 | Reference (Sphere) ⁴ | 21.9 | 14.1 | 16.9 | 3 | 0.990 |
| | | | | Hansen-type | 21.3 | 13.7 | 16.4 | 5 | 0.973 |
| | | | | Convex Hull | 17.5 | 10.6 | 14.6 | na | na |
| | | | | Axis-Aligned Ellipsoid | 18.1 | 11.8 | 15.7 | 4 | 0.974 |
| | | | | Rotated Ellipsoid | 17.8 | 11.2 | 14.6 | 6 | 0.945 |
| | | | | Ellipsoid: CHCV ³ | 17.5 | 10.6 | 14.6 | 12 | 0.758 |
| | | | | Minimum Enclosing Ellipsoid | 17.7 | 10.8 | 15.4 | 8 | 0.894 |
| ¹ Results from Sphere program provided by Nynäs | | | | | | | | | |
| ² Not Applicable | | | | | | | | | |
| ³ CHCV - Convex Hull Center and Volume | | | | | | | | | |
| ⁴ Results from Hansen (2000) | | | | | | | | | |

Table 4. Summary of Solubility Samples Examined

| Sample Material | Solvent | Concentration | Reference/Cell | Background |
|---|---|--|---------------------------------------|---|
| AAD-1, AAG-1, AAM-1 | CS ₂ Toluene Cyclohexane Isooctane | 0.1%, 1.0%, 10% | Air/cells: 0.05 mm | CS ₂ Toluene Cyclohexane Isooctane |
| CS ₂ Toluene Cyclohexane Isooctane Heptane | CS ₂ Toluene Cyclohexane Isooctane Heptane | 0.1%,1.0%,10% | Air/cells: 0.05 mm | CS ₂ Toluene Cyclohexane Isooctane Heptane |
| CS ₂ Toluene Cyclohexane Isooctane Heptane | None | N/A | Air/cells: 0.05 mm, 0.11 mm | Air |
| AAD-1 and AAM-1 maltenes | Cyclohexane | 10% | Air/cells: 0.05 mm | Cyclohexane |
| AAD-1 | Toluene and Isooctane Mixture (Heithaus ratio) | 0%, 25%, 50%, 75% | Air/cells: 0.05 mm, 0.11 mm | Toluene and Isooctane Mixture (Heithaus ratio) |
| AAD-1 Addition of carbon black at 5% wt of bitumen | Toluene and Isooctane Mixture (Heithaus ratio) | 0%, 25%, 50%, 75% | Air/cells: 0.05 mm, 0.11 mm | Toluene and Isooctane Mixture (Heithaus ratio) |
| Heptane | Cyclohexane | 0%, 1%, 10%, 25%, 50%, 75%, 90%, 99%, 100% | Air/cells: 0.05 mm, 0.11 mm | Air |
| AAD-1 asphaltenes | Toluene and Heptane Mixture (Heithaus ratio) | 0%, 25%, 50%, 75% | Air/cells: 0.05 mm, 0.11 mm, 0.021 mm | Toluene and Heptane Mixture (Heithaus ratio) |
| AAD-1 asphaltenes Addition of carbon black at 5% wt of bitumen | Toluene and Heptane Mixture (Heithaus ratio) | 0%, 25%, 50%, 75% | Air/cells: 0.05 mm, 0.11 mm, 0.021 mm | Toluene and Heptane Mixture (Heithaus ratio) |

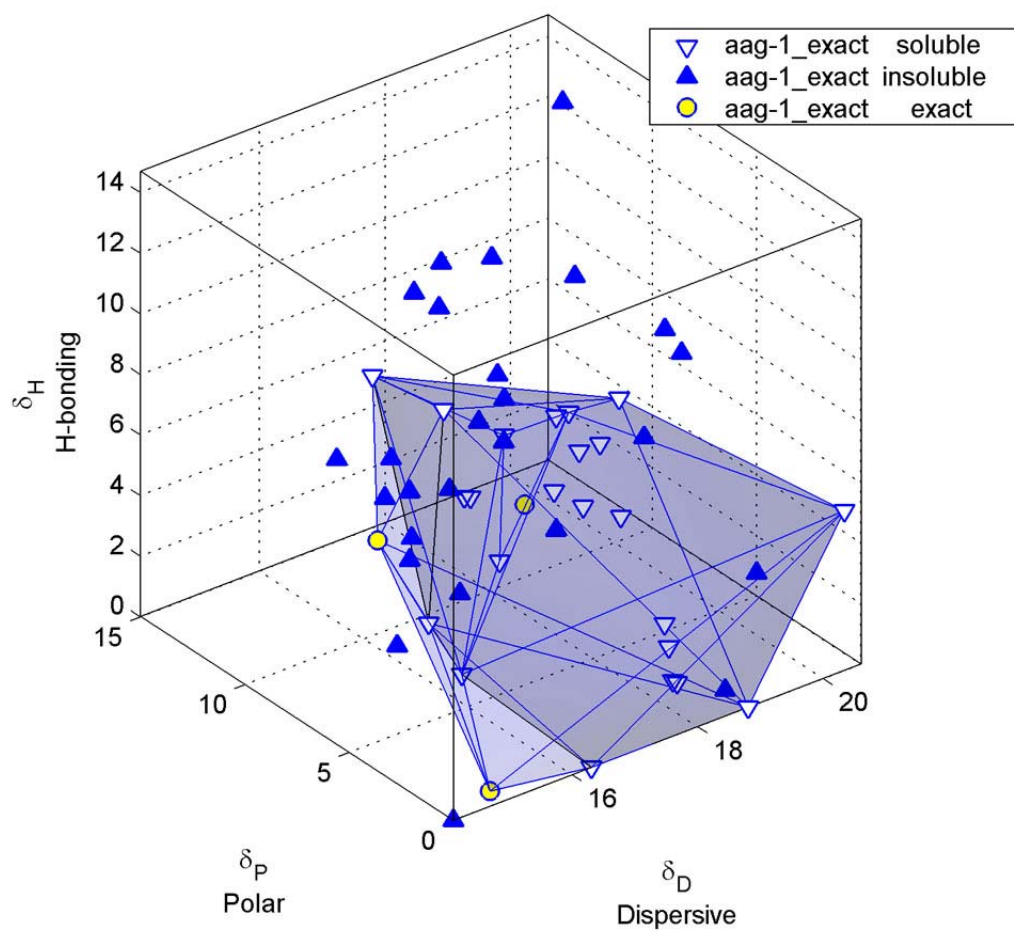


Figure 1. Convex hull fits for bitumen AAG-1 with and without “exact” points.

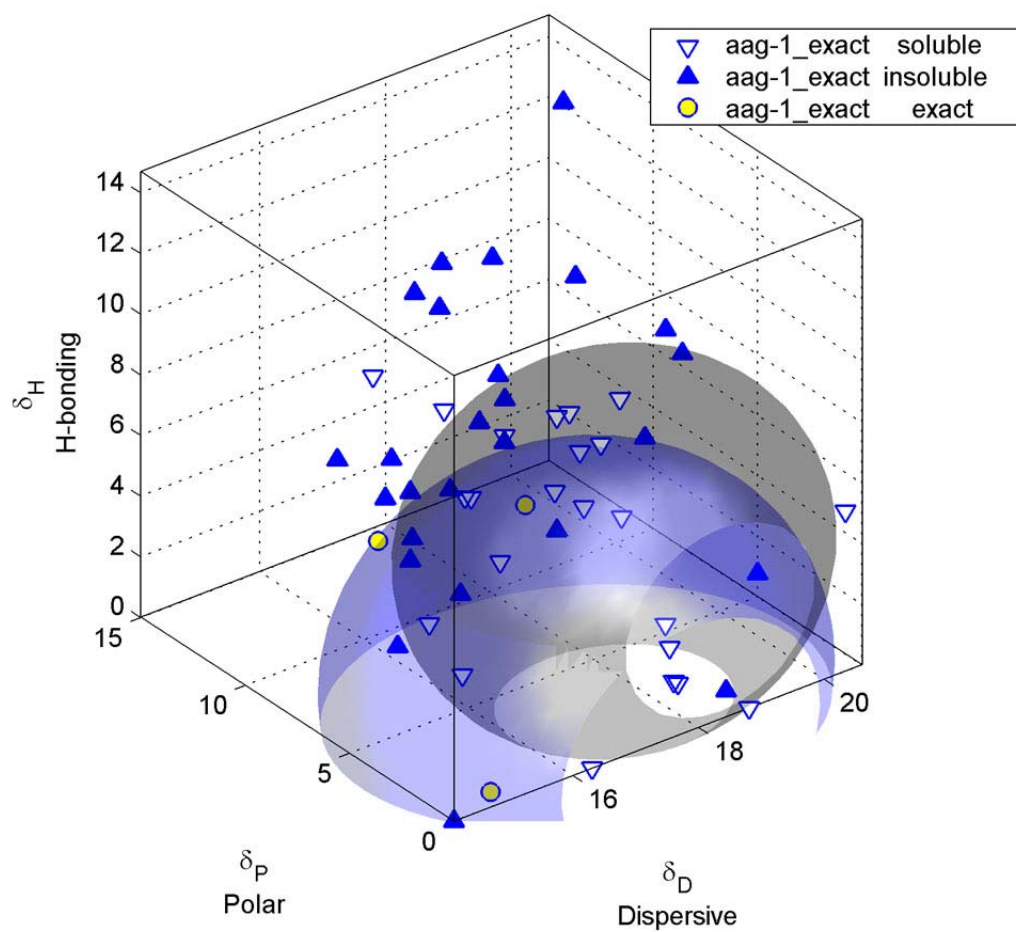


Figure 2. Hansen-type fits to bitumen AAG-1 with and without “exact” points.

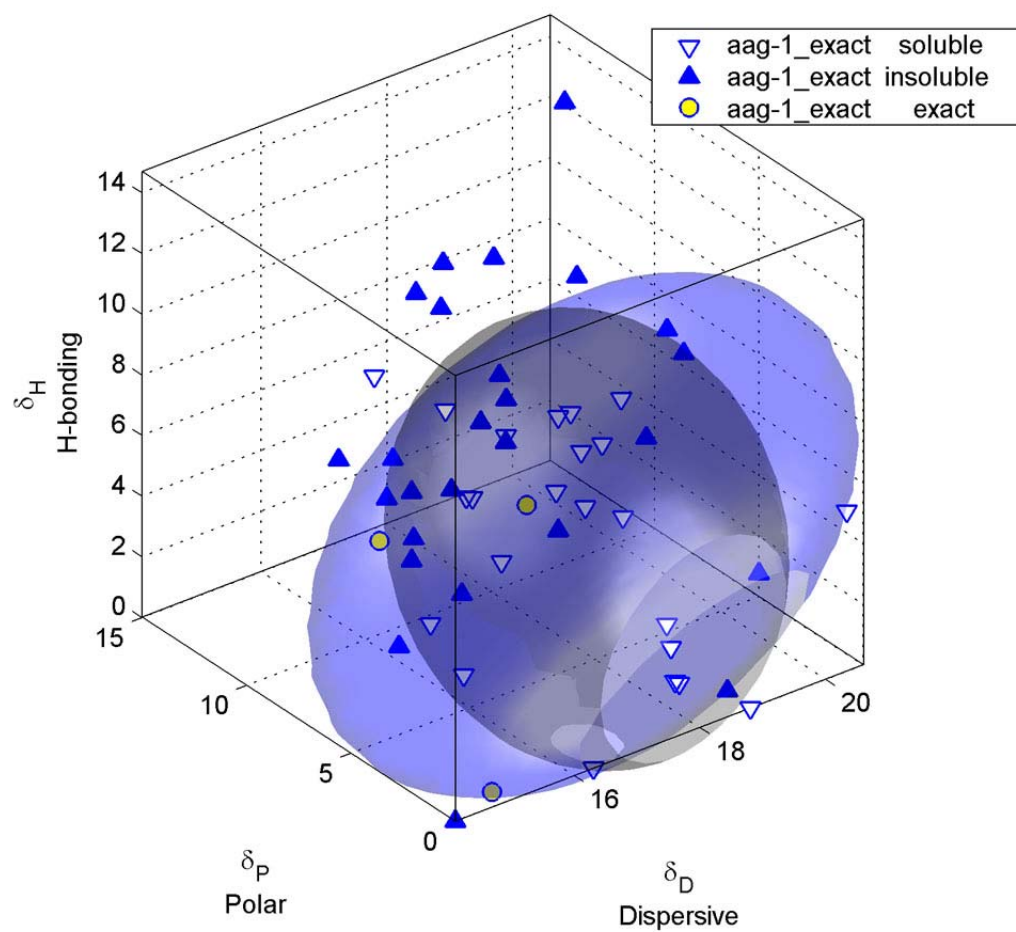


Figure 3. Rotated ellipsoid fits to bitumen AAG-1 with and without “exact” points.

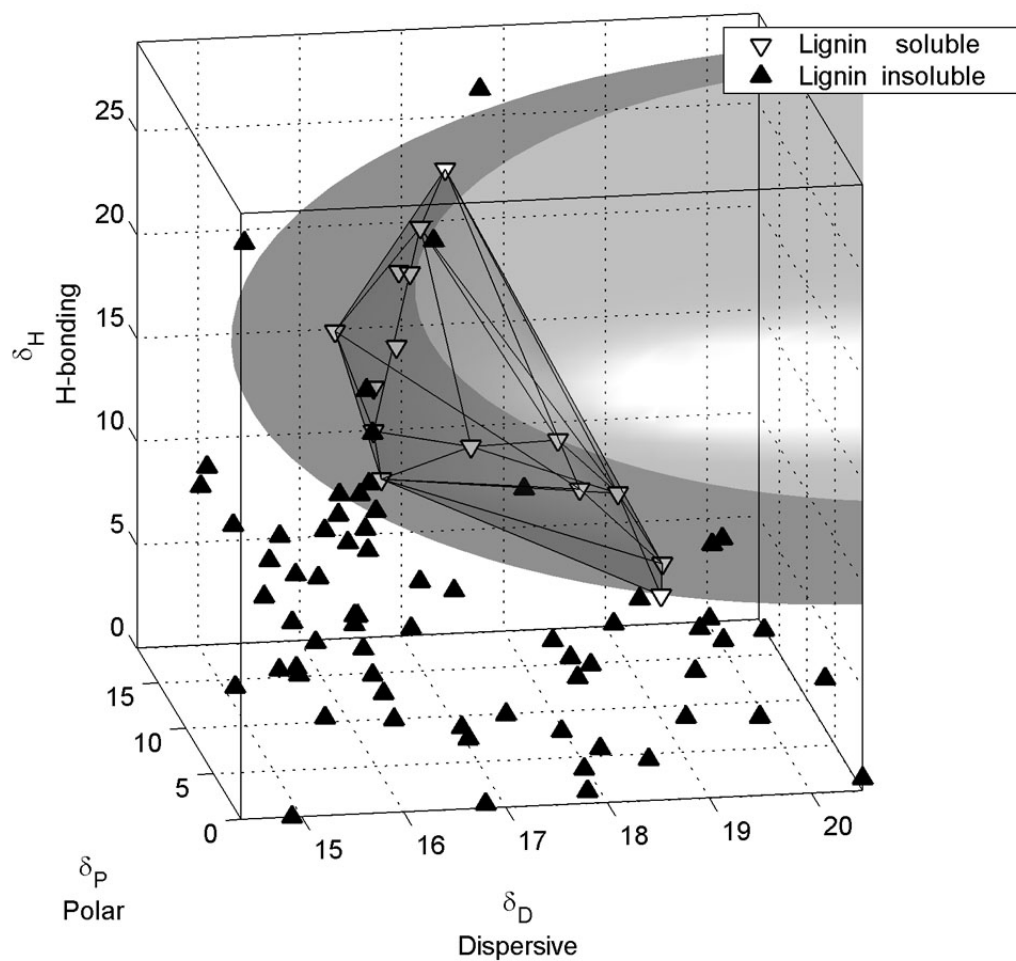


Figure 4. Convex hull and Hansen-type fits to lignin (Hansen 2000).

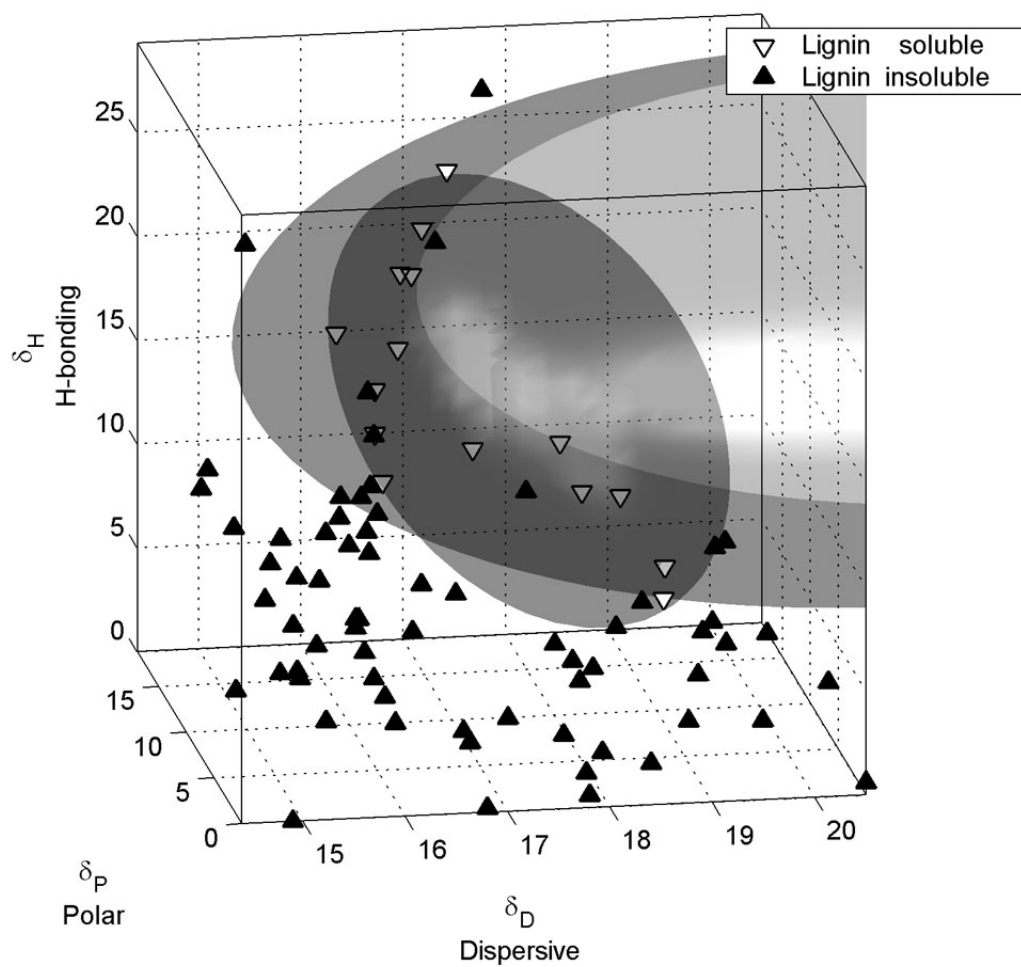


Figure 5. Rotated ellipsoid and Hansen-type fits to lignin (Hansen 2000).

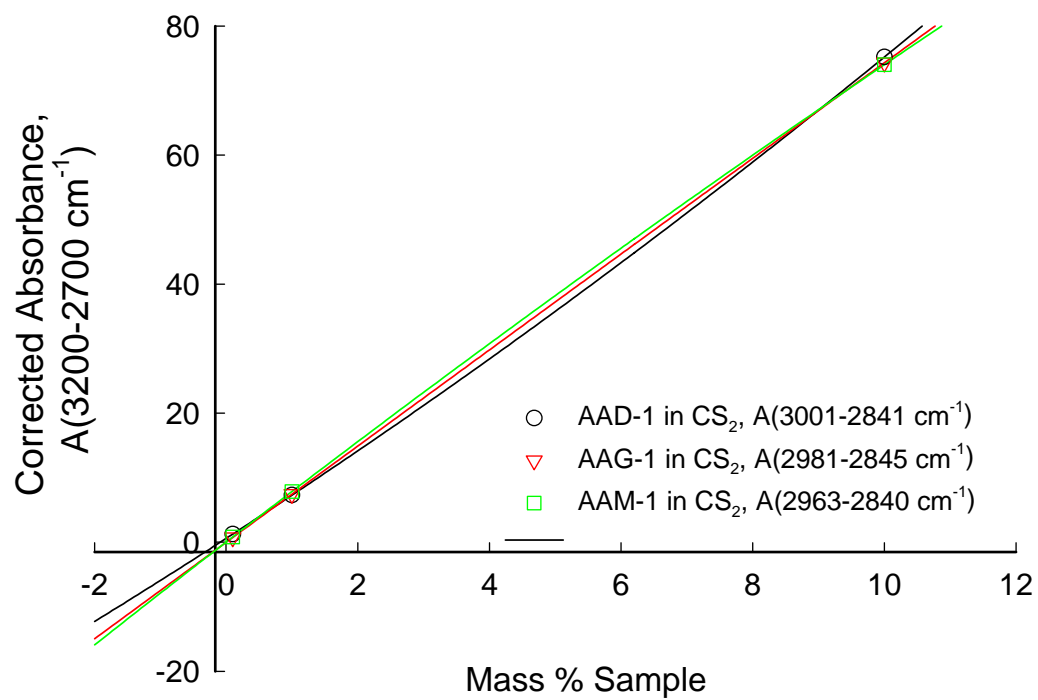


Figure 6. IR adsorption spectra (narrow CH-band peak) of bitumen AAD-1 prepared in CS_2 .

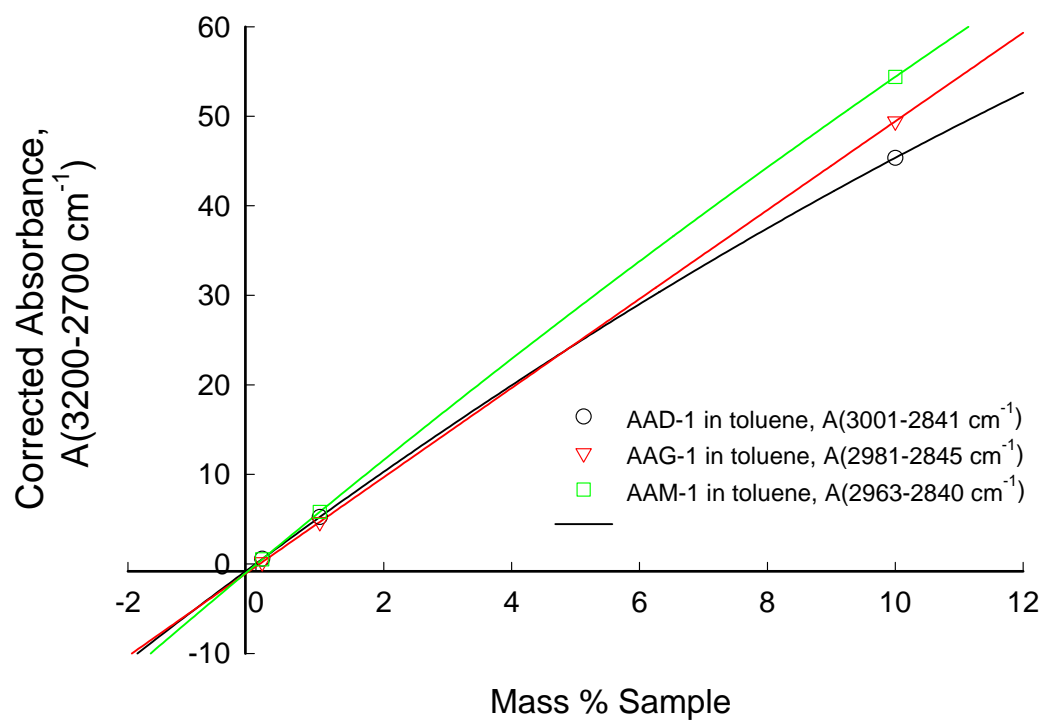


Figure 7. IR adsorption spectra (narrow CH-band peak) of bitumen AAD-1 prepared in Toluene.

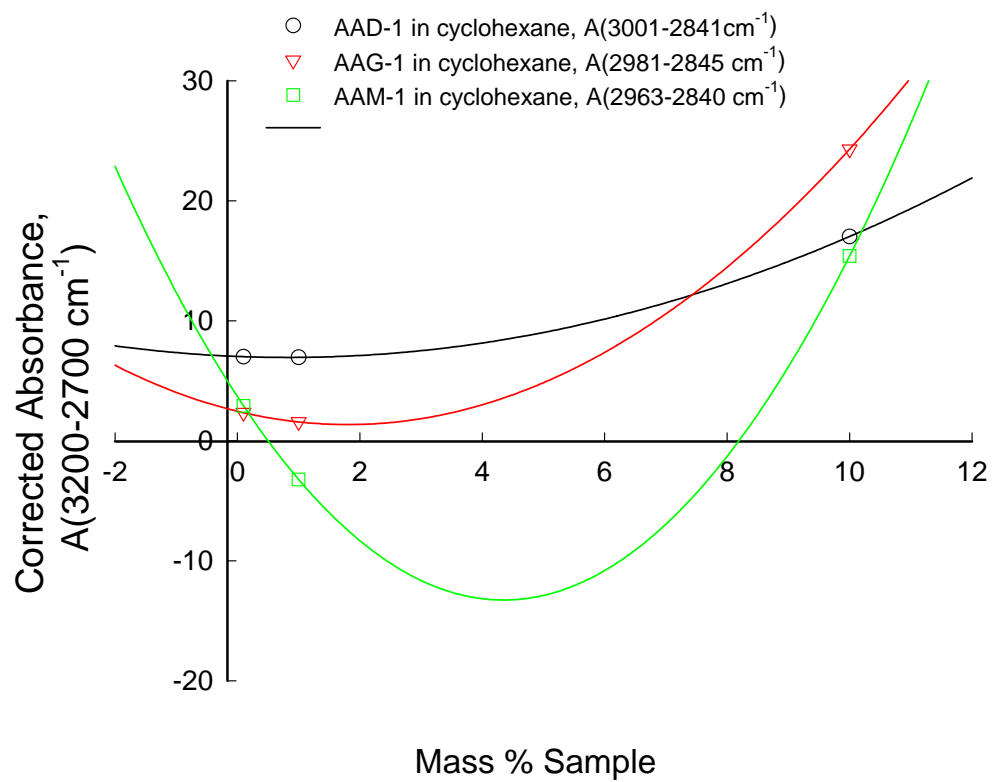


Figure 8. IR adsorption spectra (narrow CH-band peak) of bitumen AAD-1 prepared in cyclohexane.

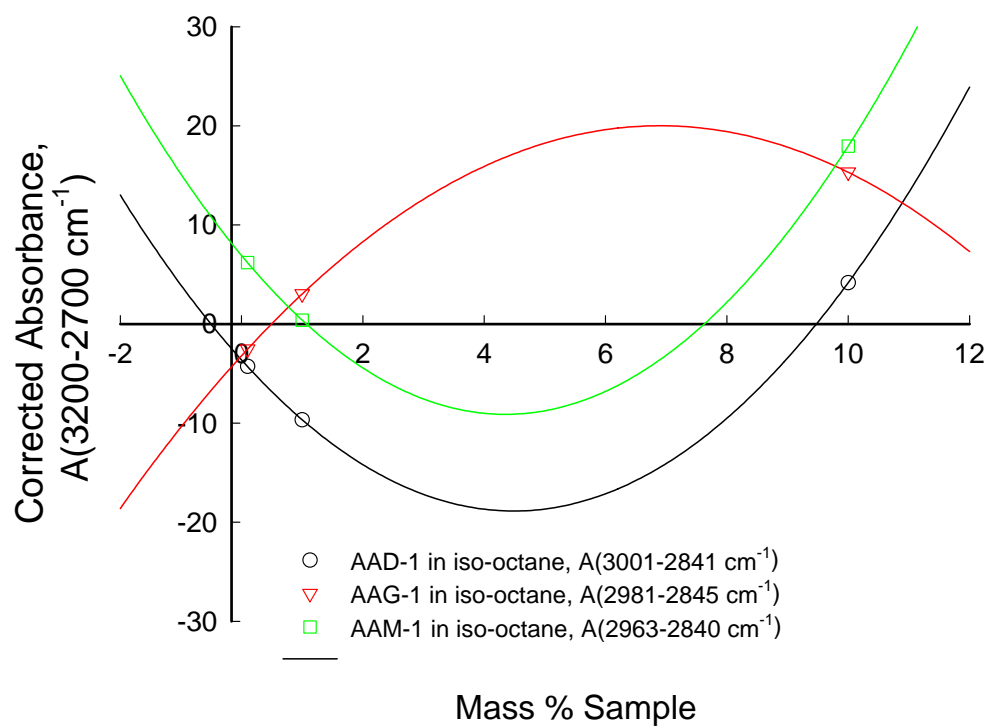


Figure 9. IR adsorption spectra (narrow CH-band peak) of bitumen AAD-1 prepared in isooctane.

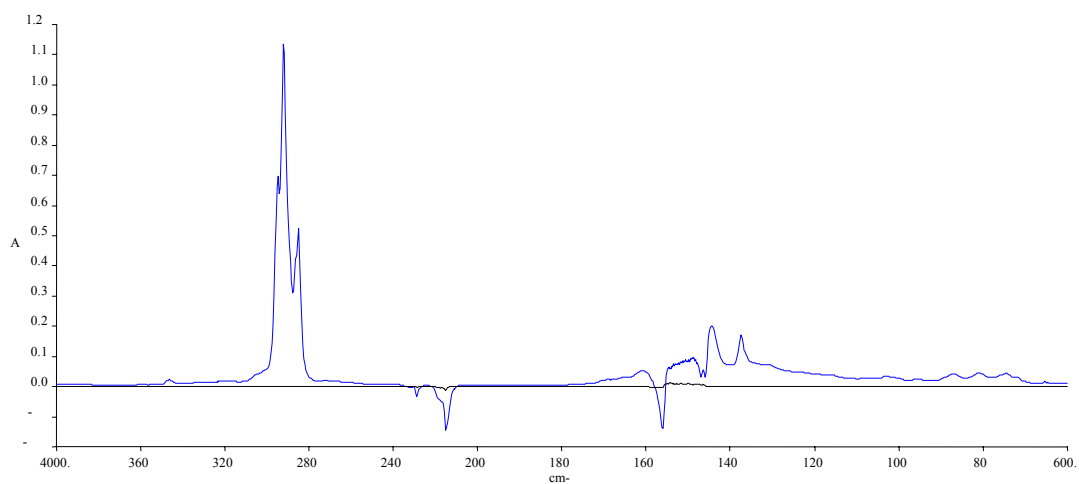


Figure 10. AAG-1 in CS₂ (blue), and CS₂ subtracted from CS₂.

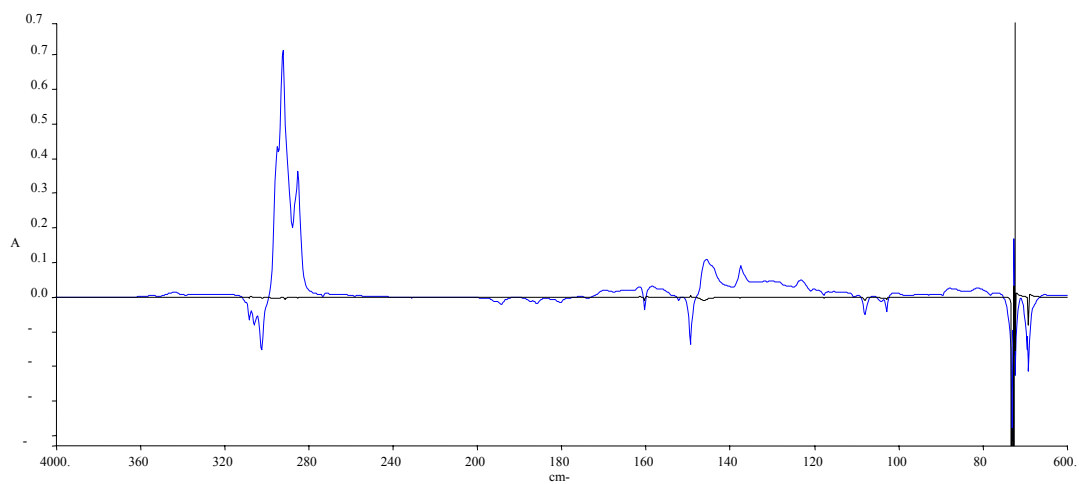


Figure 11. AAG-1 in toluene (blue), and toluene subtracted from toluene (black).

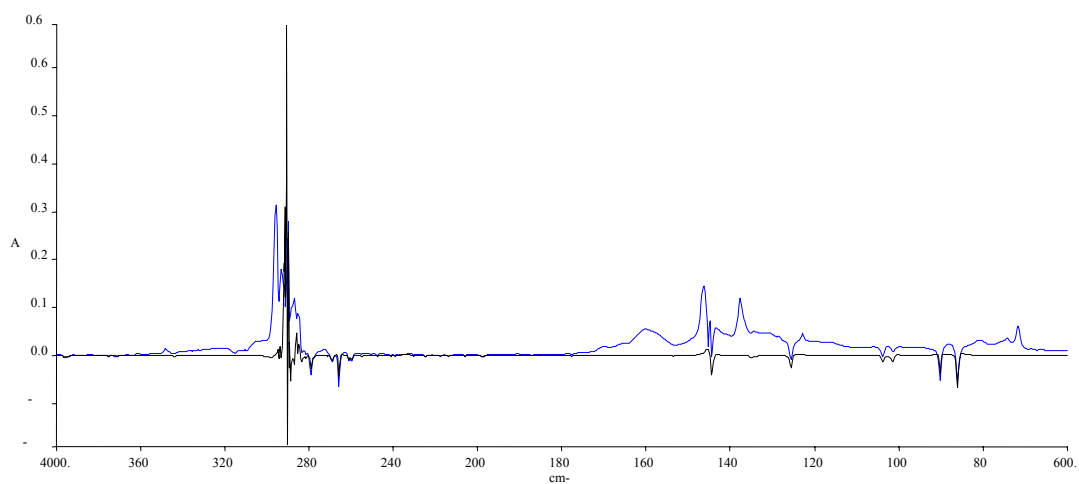


Figure 12. AAG-1 in cyclohexane (blue), and cyclohexane subtracted from cyclohexane (black).

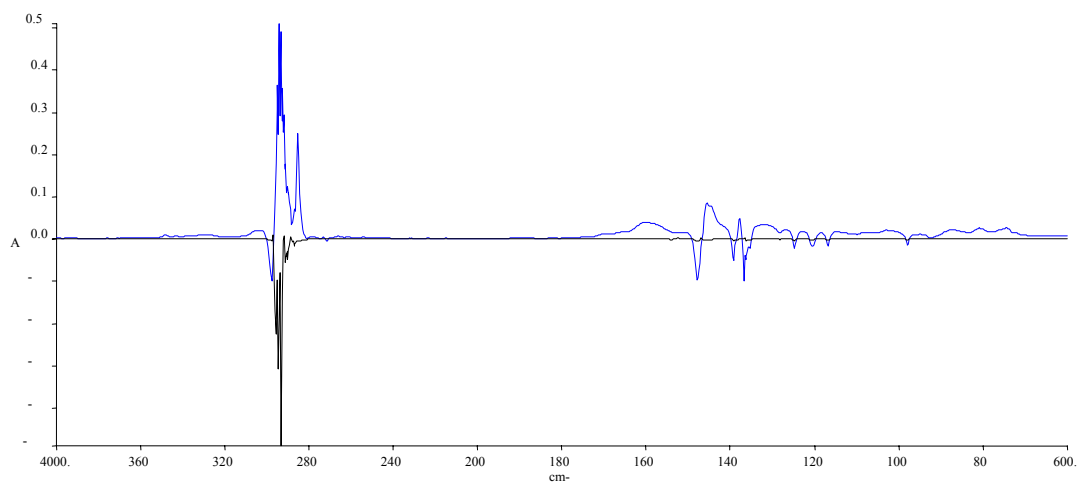


Figure 13. AAG-1 in isooctane (blue), and isooctane subtracted from isooctane (black).

Date: 7/6/2003

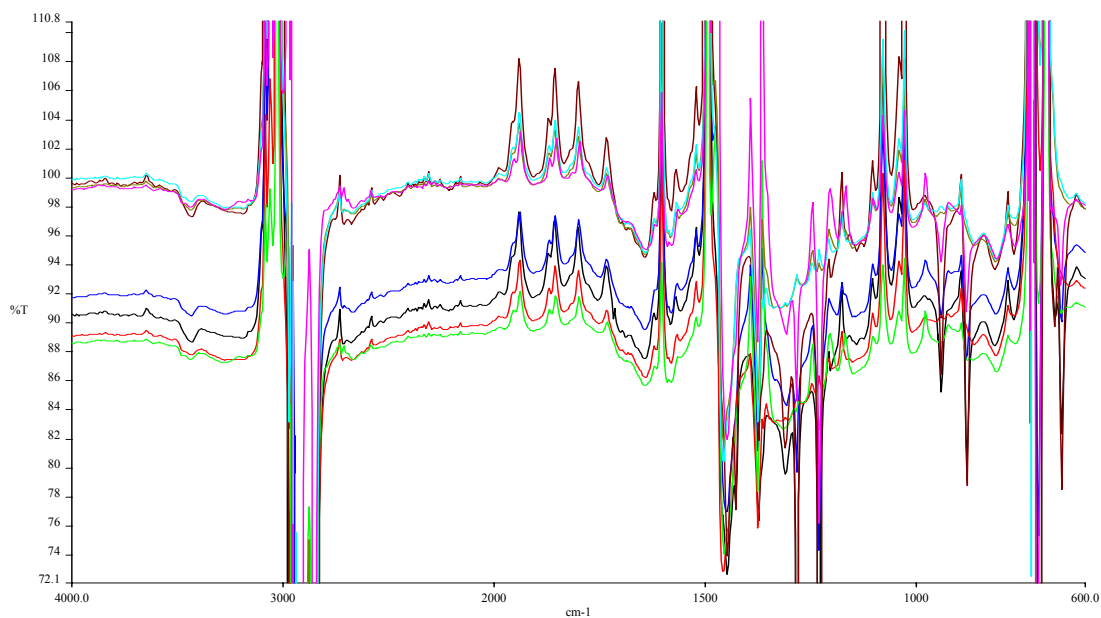
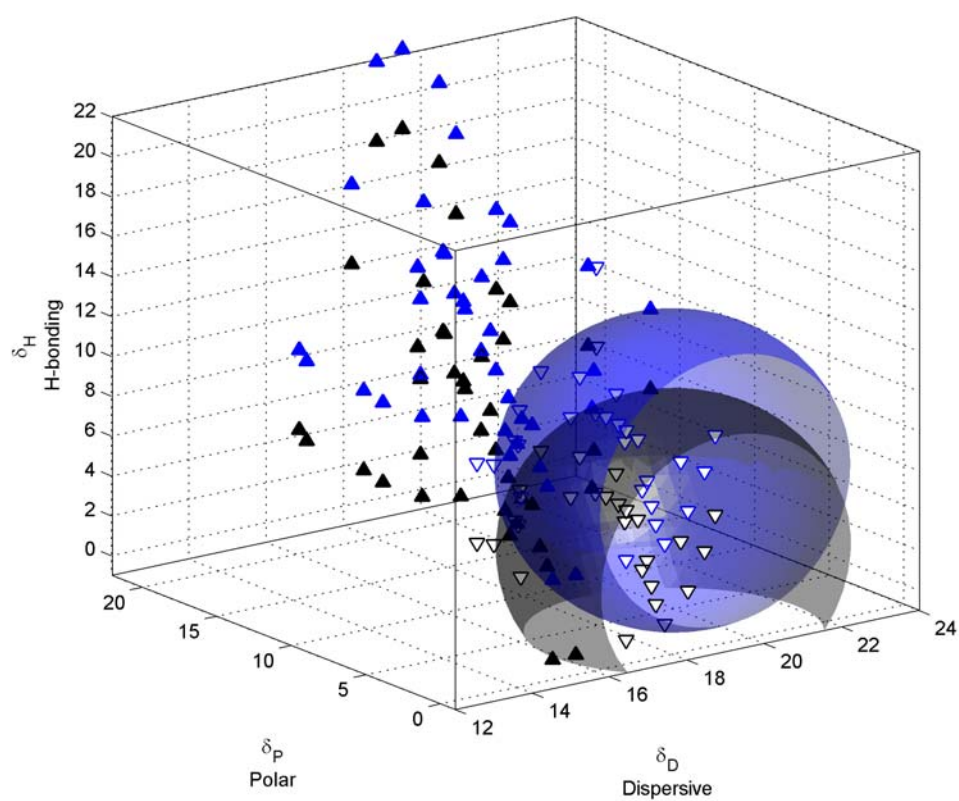


Figure 14. Percent transmittance spectra of the baseline of bitumen AAD-1 prepared in toluene, with (lower set of spectra) and without (upper set of spectra) 5% (wt/wt-sample) activated carbon.

APPENDIX



Solubility Parameter Visualization Software



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INTRODUCTION

sp3d is a software utility for viewing, plotting, and analyzing multidimensional solubility parameter data. Western Research Institute is developing the program with joint support from AB Nynäs Petroleum, Nynäshamn, Sweden, and the U.S. Department of Energy, Federal Energy Technology Center, Morgantown, West Virginia (Contract DE-FC26-98FT40323).

Understanding multidimensional techniques and their application to petroleum residues requires theoretical and historical background (taken primarily from Schabron et al. 2001). The dissolution of a material in a solvent, or the mixing of two liquids to form a single phase solution, will occur if the free energy of the process is zero or negative as described by the following equation:

$$\Delta G = \Delta H - T\Delta S$$

where ΔG is the free energy, ΔH is the heat of mixing, T is the temperature, and ΔS is the change in entropy. Typically in a dissolution process, the entropy term is relatively large, and the heat of mixing determines if the mixing will occur (Burrell 1955). Hildebrand described this heat of mixing as:

$$\Delta H = V ((\Delta E_1/V_1)^{1/2} - (\Delta E_2/V_2)^{1/2})^2 \Phi_1 \Phi_2$$

where ΔH is the heat of mixing, V is total volume, ΔE_x is the molar energy of vaporization of component x , V_x is the molar volume of component x , and Φ_x is the volume fraction of component x in the solution (Hildebrand et al. 1970). The term $(\Delta E/V)^{1/2}$ is called the solubility parameter δ , and is typically given in units of $(\text{cal/cc})^{1/2}$, called the Hildebrand in the United States, and units of $\text{MPa}^{1/2}$ elsewhere (SI units, numerically 2.0455 times larger). Numerical values for the solubility parameter of a solvent can be calculated as:

$$\delta = (\Delta E/V)^{1/2}$$

from the molar energy of vaporization to the ideal gas state, ΔE , and the molar volume V . Other means of estimating solubility parameters have been described (Hildebrand et al. 1970) and for large molecules or polymeric systems, group contributions can be used for calculation of the solubility parameter if the density of the material is known or can be estimated (Small 1953).

The heat of mixing two materials is dependent on the difference between their solubility parameters squared, $(\delta_1 - \delta_2)^2$. If the solubility parameters are identical, the heat of mixing is zero and the dissolution/mixing process is driven by the entropy term $T\Delta S$ alone; mixing will occur. If the solubility parameters are not identical, the term $(\delta_1 - \delta_2)^2$ will have a net positive value which will cause the energy term ΔH to oppose the entropy term. If the entropy term is less than the energy term, mixing or dissolution will not occur.

The use of the solubility parameter is complicated by the presence of dipole and hydrogen bonding interactions. For solvents and materials with strong polarity and hydrogen bonding components, dissolution is not predictable by the single component, or dispersion solubility parameter described above. Two component and three component solubility parameter systems have been described (Hansen 1967, Barton 1974, Wiehe 1996). For such systems, solubility is maximized when all the various components for the solvent and material being dissolved are as similar as possible. Two or three-dimensional maps are used to describe so-called solubility zones, areas, or spheres for such systems.

The Hansen (1967) approach assumes that there are three major influences on the solubility parameter: dispersive, polar, and hydrogen bonding. This approach defines the overall solubility parameter, δ (equivalent to the Hildebrand solubility parameter), as:

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

where the D, P, and H subscripts denote contributions from the dispersive, polar, and hydrogen-bonding forces, respectively.

In a recent study, Redelius (2000) used Automated Flocculation Titrimetry[®] (AFT[®]) (see below) results to demonstrate the need and desirability of using multidimensional solubility parameters to adequately model petroleum residua solubility. He describes a 3-dimensional stability space expressed in terms of Hansen solubility parameters. By monitoring changes in this space, his model allows prediction of residuum stability and the calculation of its sensitivity to different processes. Examples of these processes are aging, oxidation, visbreaking, and fluxing or blending residua.

The solubility space described by Redelius (2000) consists of three axes corresponding to the δ_D , δ_P , and δ_H directions. The solubility of a petroleum residuum is measured in a variety of solvents whose three-component solubility parameters are known. Thus, each solvent provides a coordinate in the solubility space and an indicator of solubility (yes or no) at that location. With enough points, a body can be defined such that most of the soluble coordinates are inside the body and most of the insoluble coordinates are outside the body. The coordinates of the center of this body are then assumed to be the average for the petroleum residuum. The number of solvents needed to define the body can be sharply reduced by performing titrations that exactly locate the body wall. sp3D was developed to incorporate exact titration data into the solubility space modeling and to provide a visual exploration tool for the data and solubility bodies.

The current version of sp3d is able to import up to three data sets to memory. The datasets consist of: solvent descriptions, solubility space coordinates, and solubility indicators. Solubility indicators can be: soluble (1), insoluble (0), or exact (-1). At present, six surface types fit the data. These are discussed in detail later in this document.

AUTOMATED FLOCCULATION TITRIMETRY[®]

Western Research Institute (WRI) has developed an automated titrimer for the accurate, reproducible determination of Heithaus (solubility-related) parameters (Heithaus 1962) in petroleum residua (Pauli 1996). This titration apparatus and method, termed Automated Flocculation Titrimetry[®] (AFT[®]), has been refined and improved, and is finding application in the characterization of petroleum residua during pyrolysis, oxidative aging, and upgrading (Pauli 1996; Pauli and Branthaver 1998, 1999; Schabron and Pauli 1999; Schabron et al. 2001a, 2001b, 2001c). With selected solvent systems, AFT[®] can be used to develop multidimensional solubility-parameter spaces for characterizing petroleum residua.

INSTALLATION

Insert the sp3D distribution CD into an available drive tray and close the tray. The sp3D installer will start automatically if the autorun feature of Windows is enabled on your computer. If the installer does not start automatically, locate the CD drive in Windows Explorer and doubleclick on the filename setup.exe located on that drive. The installer will then lead you through the install process shown below.

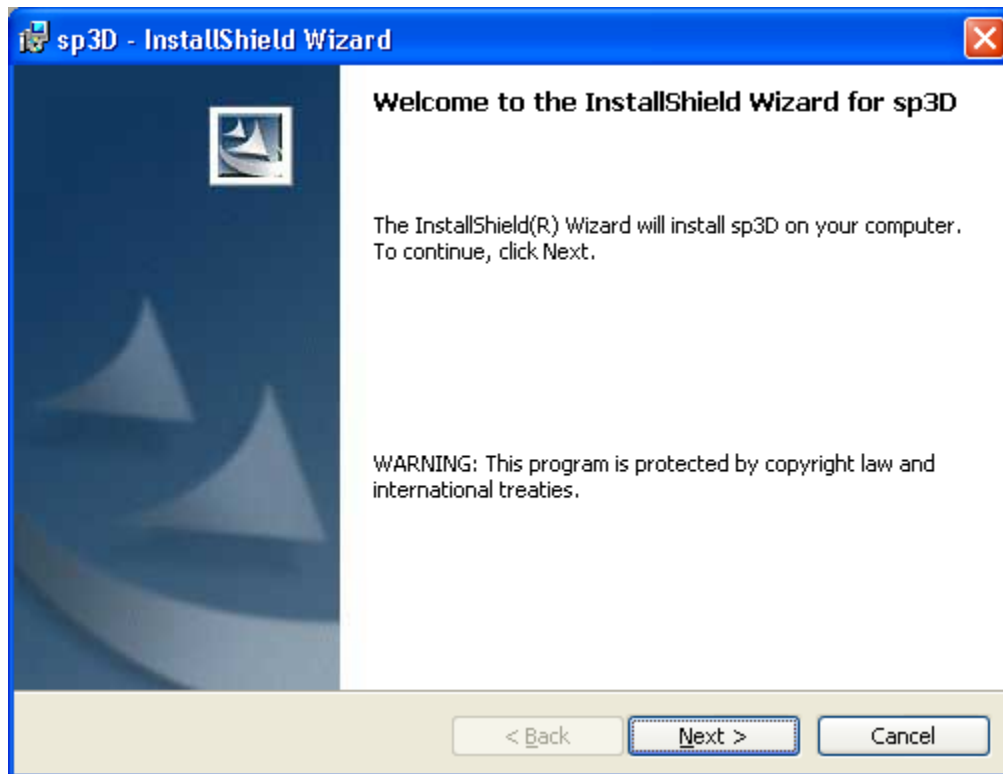


Figure 1. InstallShield Opening Window

Click on “Next >” to continue installation.

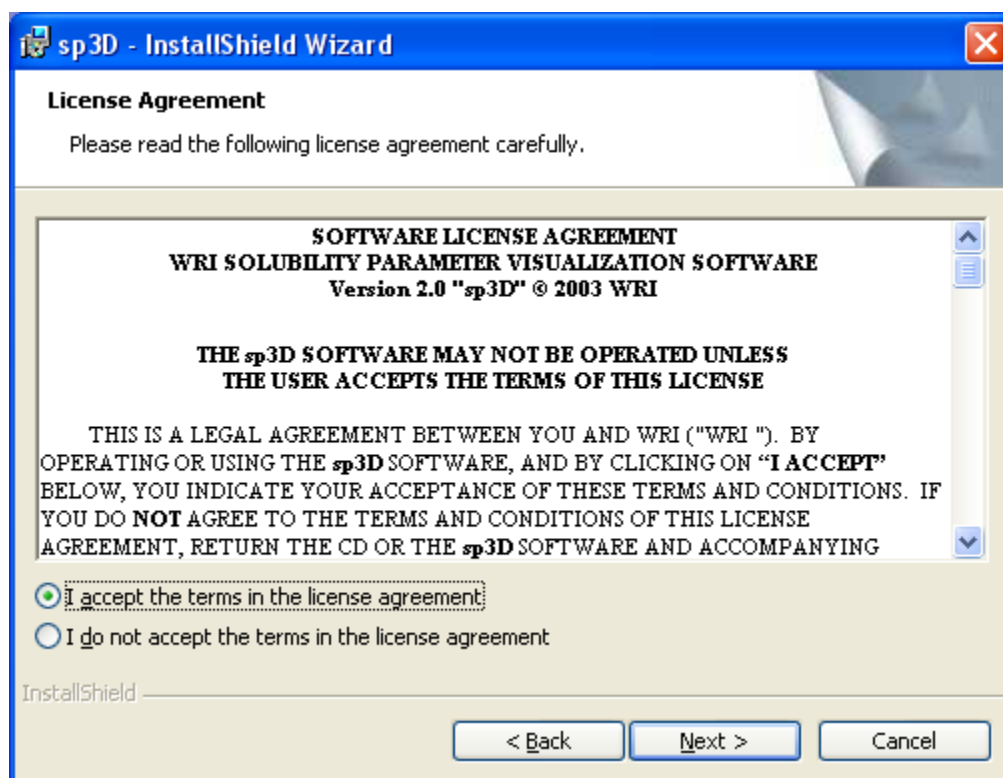
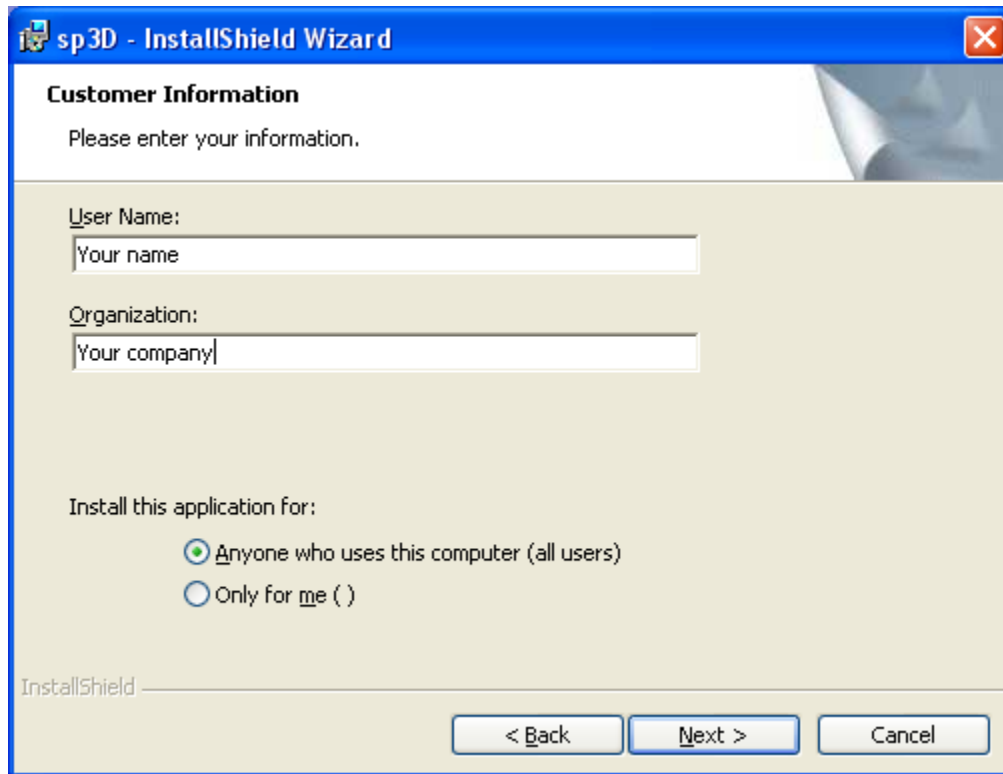


Figure 2. License Agreement

Figure 2 shows a typical click-license agreement for version 2.0 and greater of the software. Content may vary..

Click on "I accept the terms in the license agreement", and then Click on "Next >" to continue installation.



The image shows a Windows-style dialog box titled "sp3D - InstallShield Wizard". The window has a blue title bar with a standard Windows icon on the left and a close button (X) on the right. The main content area has a light beige background. At the top, the text "Customer Information" is displayed in bold. Below it, a smaller line of text says "Please enter your information." The form contains two text input fields: the first is labeled "User Name:" with a placeholder "Your name"; the second is labeled "Organization:" with a placeholder "Your company". Below these fields, there is a section titled "Install this application for:" followed by two radio button options. The first option, "Anyone who uses this computer (all users)", is selected with a green dot. The second option, "Only for me ()", is unselected. At the bottom left of the dialog, the text "InstallShield" is visible. At the bottom right, there are three buttons: "< Back", "Next >", and "Cancel". The "Next >" button is highlighted with a blue border.

Figure 3. Customer Information

Enter your name and organization. Default values will be obtained from your computer, but you can enter new information. Click on “Next >” to continue installation.

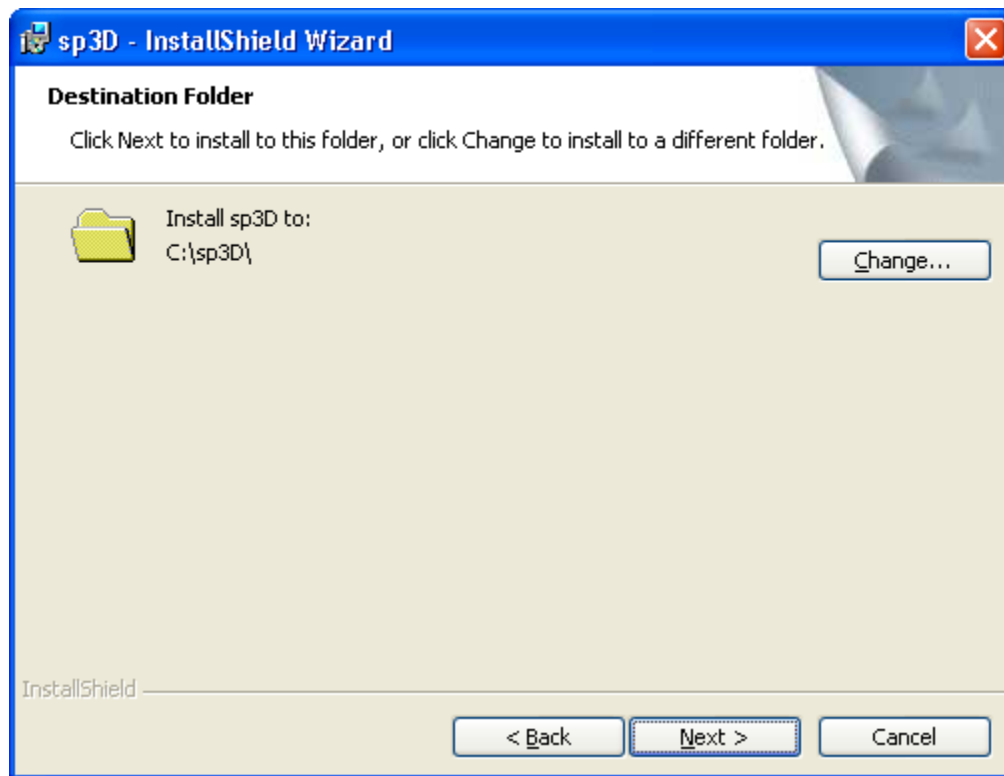


Figure 4. Select Installation Folder

Accept or change the installation folder. Leave this at the default value unless absolutely necessary. Click on “Next >” to continue installation.



Figure 5. Review Installation Settings.

Review your installation information. Click on "< Back" to change values. Click on "Install" to continue installation.

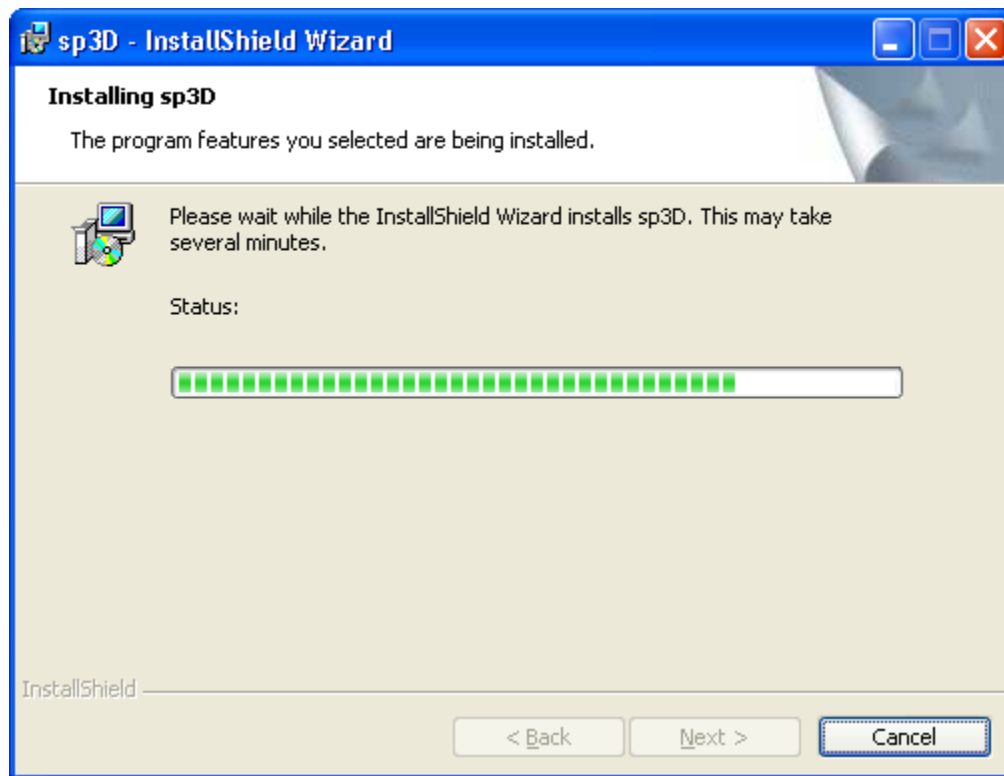


Figure 6. Installation Progress Window

InstallShield will now install sp3D on your computer. Please be patient while all files and settings are installed.

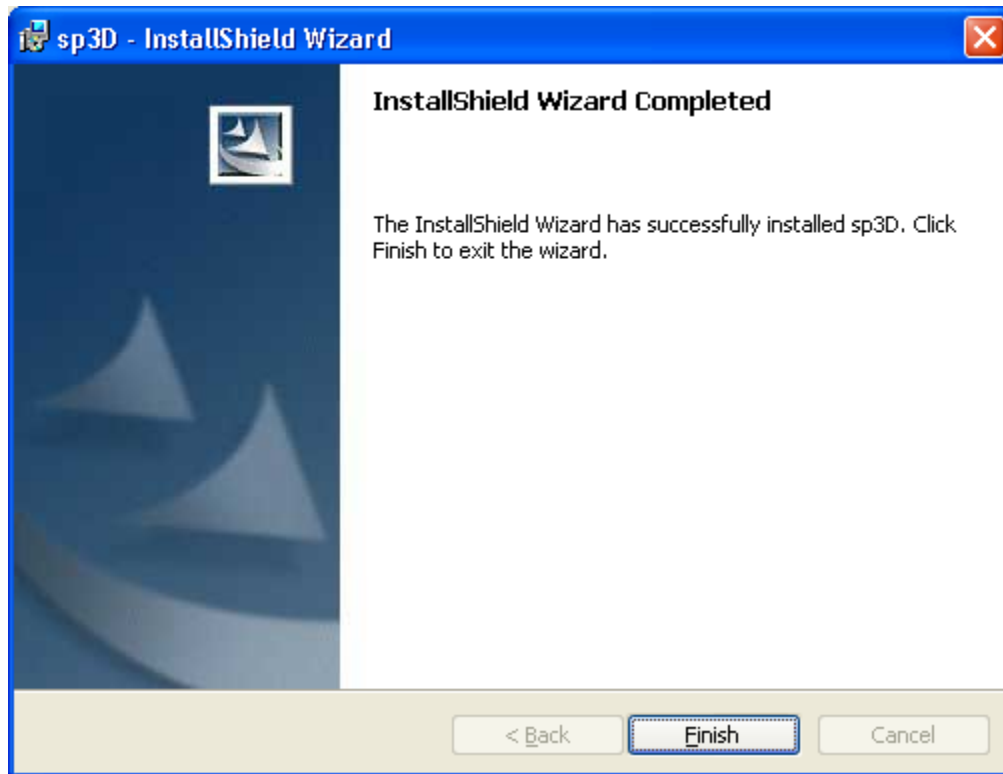


Figure 7. Installation Complete Window

When installation is completed, the above message will be displayed. Click on “Finish” to continue installation. If you are using Windows 9x or Me, it is critical that your computer be “rebooted” to finish the setup process. Please close all Windows programs and “reboot” or click on “Yes” in the message window.

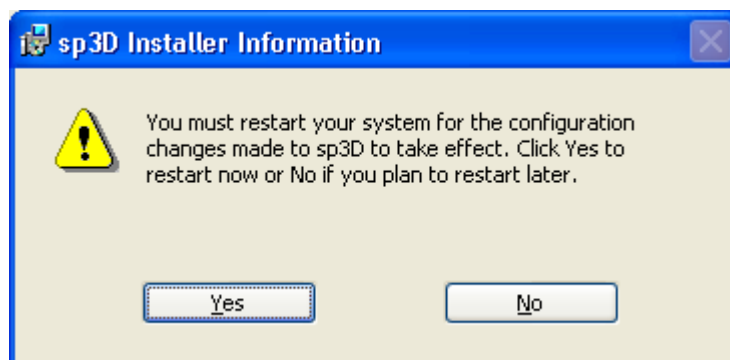


Figure 8. System Reboot Message

OPERATION

Find and double click on the sp3D shortcut icon on your desktop or select sp3D in your program list. sp3D is a simple program to operate. It employs a graphical user interface (GUI) to control most of the display and calculation features. The opening figure shows an empty solubility space awaiting user input.

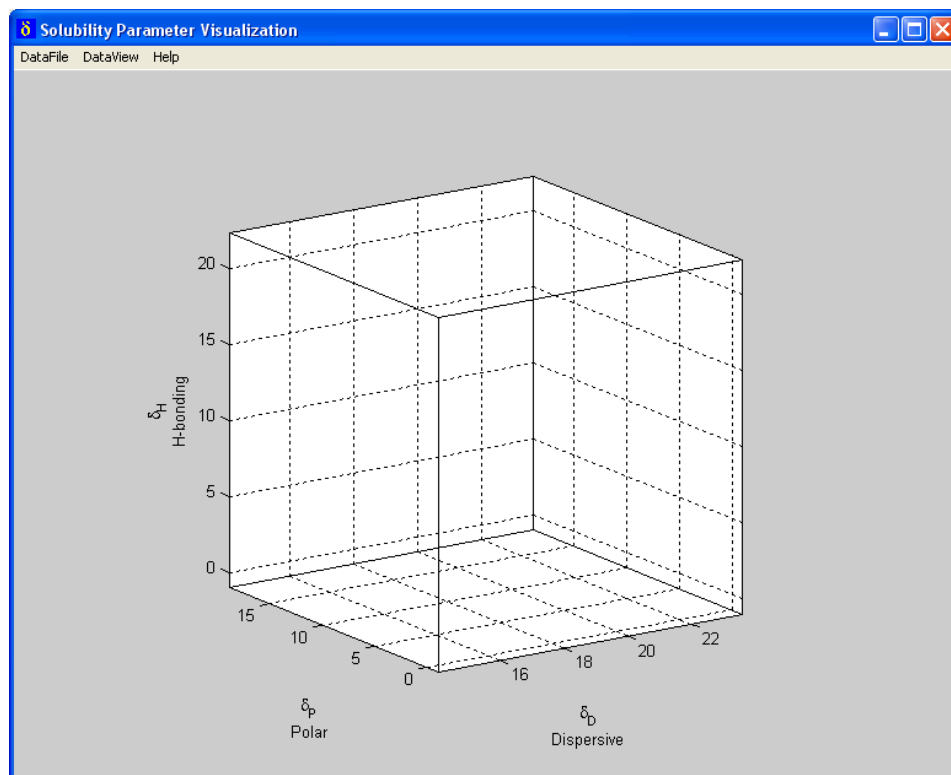


Figure 9. sp3D Opening Figure

At this point, only a limited number of actions are allowed. Clicking on the “DataFile” menu, as shown in the next figure, displays the available options for opening files, setting graphical preferences, and exiting the program (see Figure 9). The menu selection for “Exit” closes sp3D. The “Preferences” selection allows the default graphics settings for data-point colors, sizes, and shapes to be changed. It also provides toggles to prevent fitting of selected surface types. This selection loads Windows NOTEPAD to edit the sp3D.ini settings file. It is not recommended that the default values be changed unless the file is first backed up. This can be accomplished by selecting “Preferences” and immediately saving the unmodified file as sp3D.bak or similar. Close the file, reselect “Preferences”, and modify the settings. Appendix A contains tables of the available graphics settings.

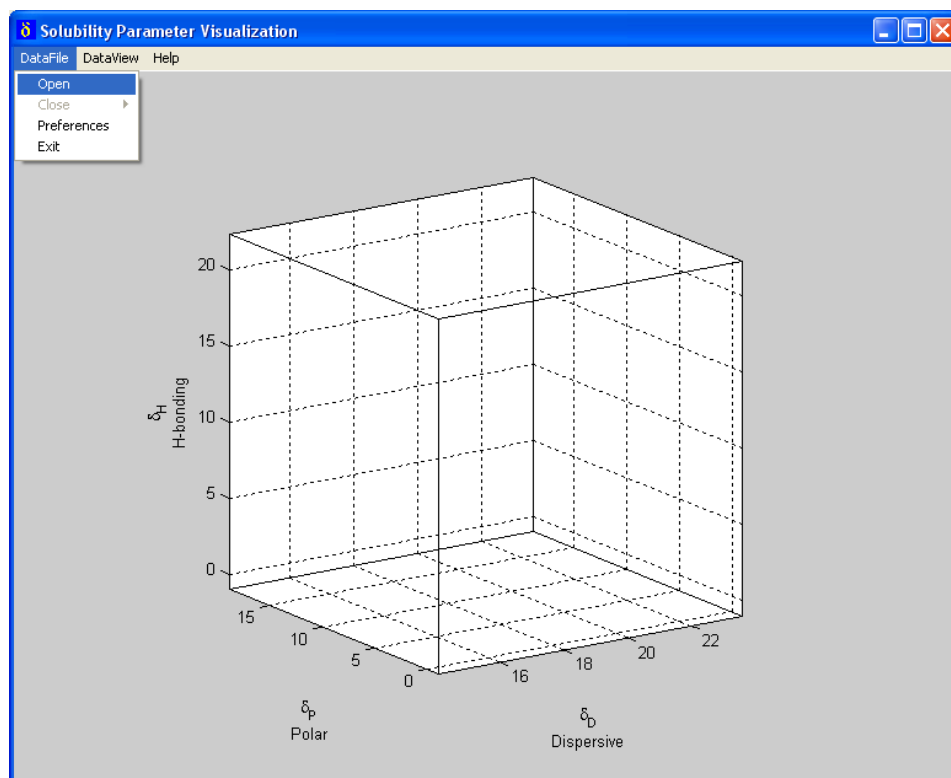


Figure 10. DataFile Menu Options

The “Open” selection on the “DataFile” menu will be discussed later. Now we will examine the initial options available from the “DataView” menu. Clicking on the “DataView” menu, as shown in Figure 10, displays the selection options for manipulating the 3D plotting space. The first option, “Rescale”, allows the manual rescaling of the three solubility axes. An example of the rescale window is shown in Figure 11. Current values are shown in the rescale window. If necessary the rescale window can be moved to allow viewing of the 3D figure. In addition, the 3D plot space can be tilted and rotated by clicking and dragging using the left mouse button while pointing at the 3D graph. This is especially useful in selecting optimum axes ranges after data or fit bodies are displayed.

Related to the “Rescale” option is the “Toggle equal axes” selection. By default, sp3D expands each axis range visually to form a cubic plot space. The “Toggle equal axes” keeps the axes limits, but displays axes on the same visual scale. Try it.

The other two selection options on the opening figure are for data export and copying. “Export current figure” requests a file name and saves the current figure to that file as a .TIF, .PNG, or .JPG image. These formats are viewable by most graphics editing programs. The “Copy current figure” selection copies the figure to the Windows clipboard. The image can then be pasted into most Windows programs (for example Word, PowerPoint, etc.).

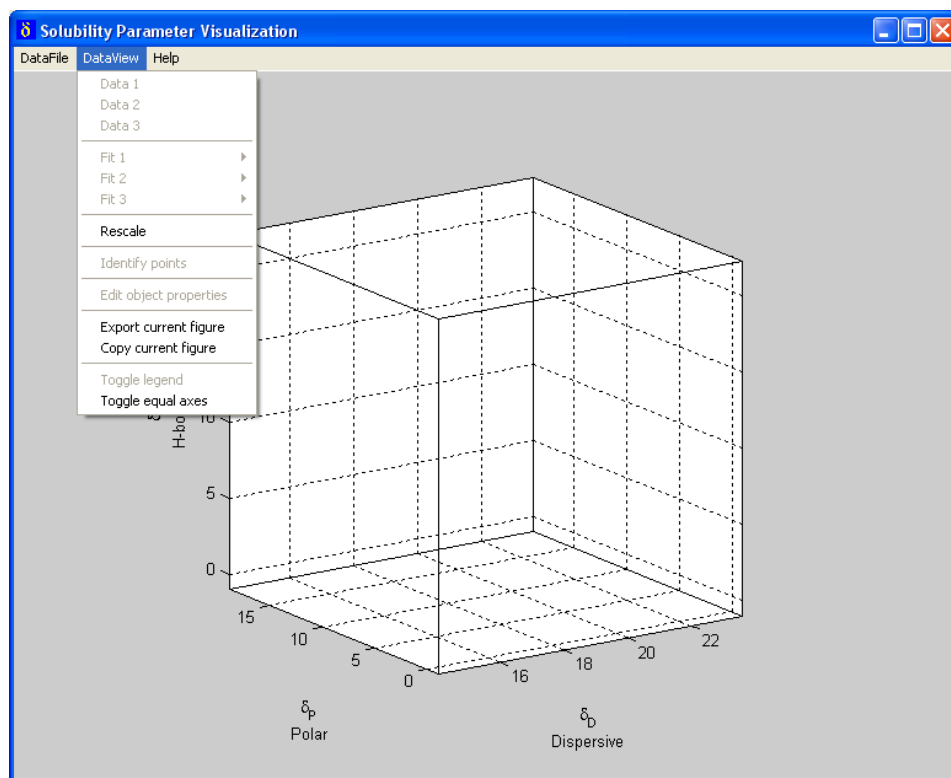


Figure 11. DataView Menu Options.

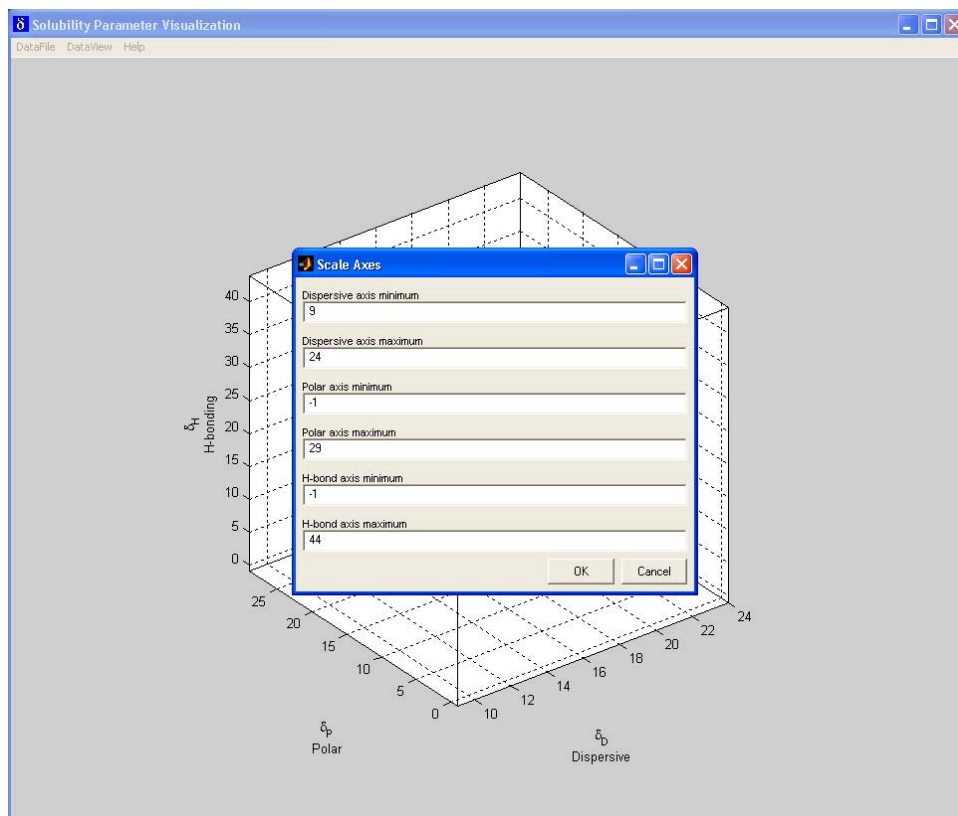


Figure 12. Manual Rescaling of Graph Axes

We will now discuss the “Open” selection on the “DataFile” menu (see Figure 9) and follow that with an example session in which we load and display data, and create solubility bodies for that data. Clicking on “Open” brings up the import data dialog shown in Figures 12 and 13. Figure 12 shows the folders in your install directory. Seven example data files can be found in the “data” folder (see Figure 13). In this discussion, we will select the file named Bitumen1Data.xls. Double-clicking on Bitumen1Data.xls (or single clicking followed by selecting the open button) opens the worksheet selection menu shown in Figure 14. Double-clicking on a sheet name (or single-clicking followed by selecting the open button) loads the data set into program memory. Text data files (*.txt) are loaded in a similar fashion, but without the data sheet selection menu. You will now be given the opportunity to rename the data set for either type of data file as shown in Figure 15.

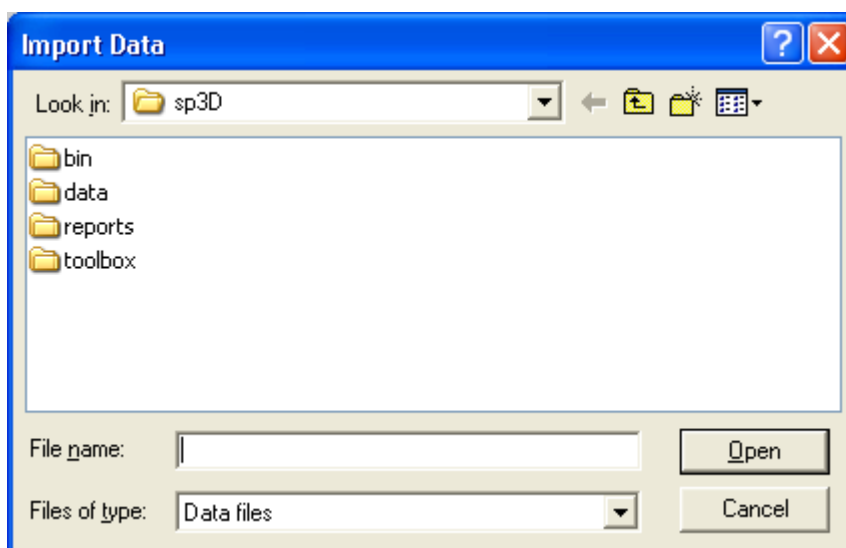


Figure 13. Install Directory Folders

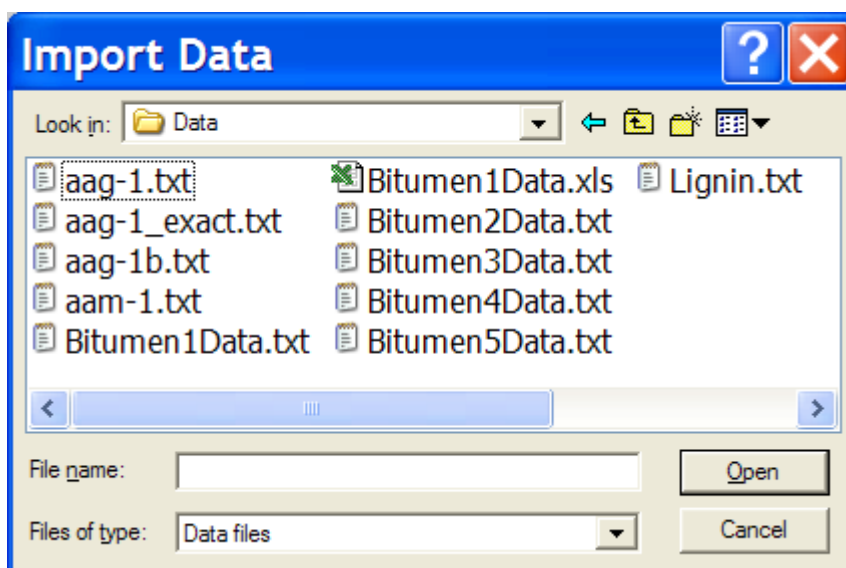


Figure 14. Example Data Files

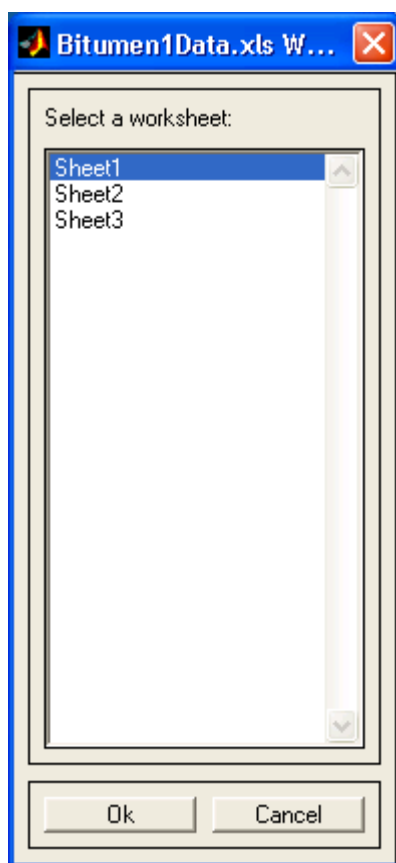


Figure 15. Excel Data Sheet Selection Menu

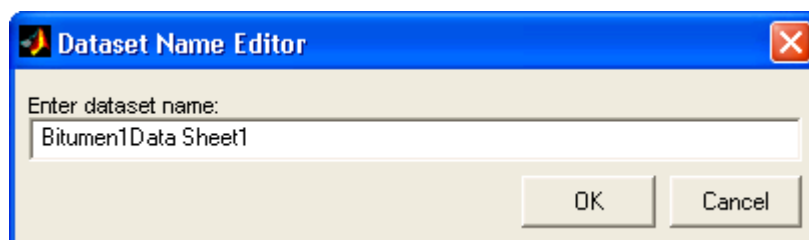


Figure 16. Dataset Name Change Menu

After loading the data and editing the dataset name, nothing will immediately appear in the figure because data import and data display are separate functions. However, we can verify that the selected data set is in memory by viewing the “DataView” menu. Clicking on “DataView” shows two new options in the menu (Figure 16). The first of these options is the data set name in the top section of the drop-down menu. Clicking on this option displays a plot of the data points in the Bitumen1DataSheet1 data set. Figure 17 shows the plotted data and also shows a check mark next to the data set name on the “DataView” menu. This check indicates that the data are plotted. Selecting the data set name again will remove the plotted data from the figure and remove the check. In this manner, any data set can be plotted or “turned off” as many times as the user desires. It is also possible, as it is at all times, to rotate and tilt the solubility space. An example is shown in Figure 18 with this data set.

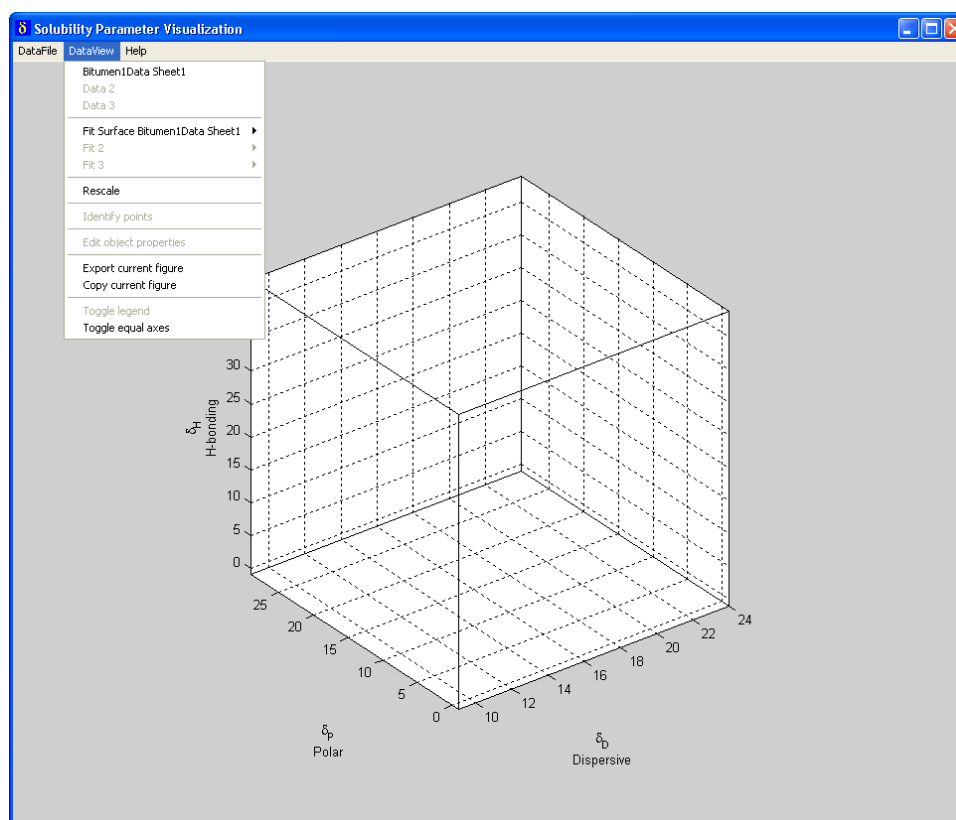


Figure 17. DataView Menu with One Data Set Loaded

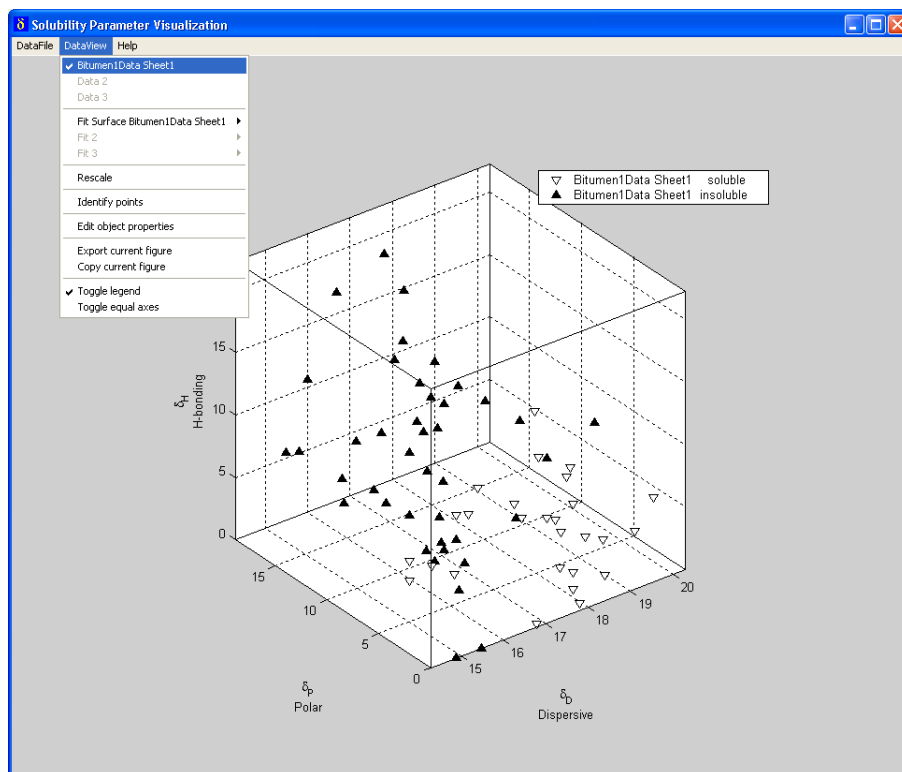


Figure 18. Dataview Menu and Plotted Data

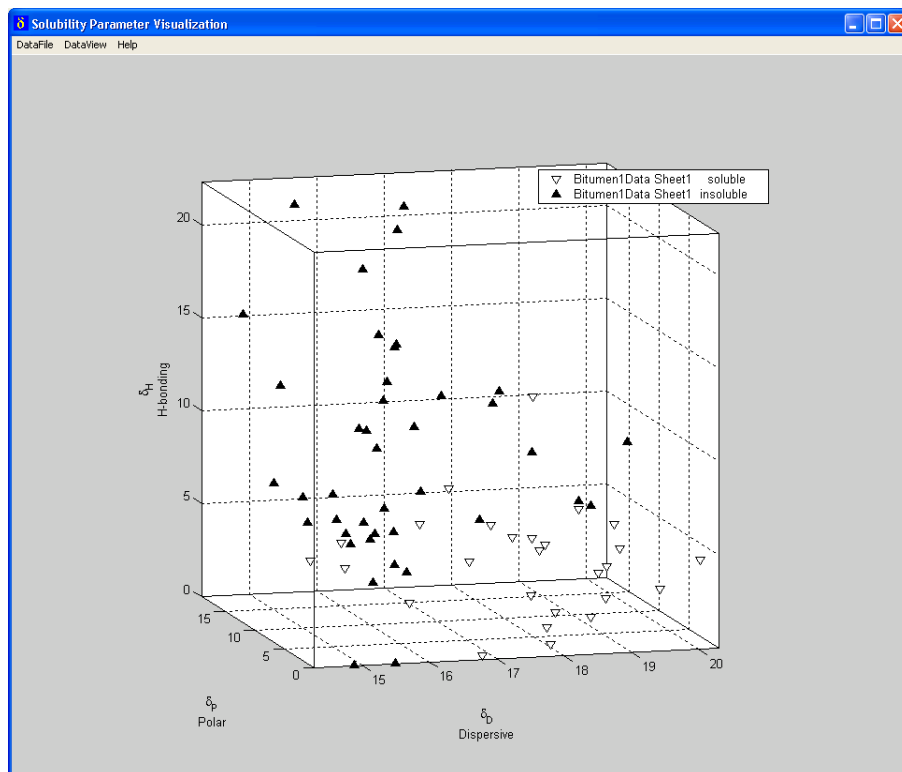


Figure 19. Rotated and Tilted Solubility Space

Other options are highlighted when a data set is plotted. These include “Identify points”, “Edit object properties”, and “Toggle legend”. These options will be discussed later.

The other “new” option on the “DataView” menu is in the second section. Here is a highlighted entry labeled “Fit Surface Bitumen1DataSheet1”. This is the access point to the most important feature of this program, the fitting of solubility surfaces to the solubility data. At present, six surfaces types are fit to the data. They are listed below in separate sections.

Convex hull

This is the surface one would see if the set of “soluble” points were wrapped with a flexible membrane. It is the smallest convex region that contains the data set. The fit is obtained through the MATLAB® implementation of the Qhull algorithm (National Science and Technology Research Center for Computation and Visualization of Geometric Structures (The Geometry Center), University of Minnesota 1993). The convex hull shows the smallest body containing the “soluble” points and is useful for examining data for overlapping regions.

Hansen-type ellipsoid

The second surface generated by the program is a modified “sphere” as is used in the well-known Hansen fit. This is actually an ellipsoidal body described by equation 1 (Hansen 2000),

$$(\text{Radius})^2 = 4(\delta_D - \delta_{D0})^2 + (\delta_P - \delta_{P0})^2 + (\delta_H - \delta_{H0})^2 \quad (1)$$

where

Radius is the apparent body radius in solubility parameter units,

δ_D and δ_{D0} are the data and body center coordinates along the dispersive axis,

δ_P and δ_{P0} are the data and body center coordinates along the polar axis,

δ_H and δ_{H0} are the data and body center coordinates along the hydrogen-bonding axis.

The variable parameters are δ_{D0} , δ_{P0} , δ_{H0} , and Radius. The quality of fit is determined identically to that described by Hansen (2000), but the search algorithm for optimum parameters is different.

Axis-aligned ellipsoid

The third surface fit to the data is simply the Hansen fit described above, but with variable coefficients on the difference terms (equation 2)

$$(\text{Radius})^2 = a(\delta_D - \delta_{D0})^2 + b(\delta_P - \delta_{P0})^2 + c(\delta_H - \delta_{H0})^2 \quad (2)$$

where

a, b, and c are the new variable parameters.

All other parameters are identical to the Hansen-type fit. This is an ellipsoid with principal axes aligned in the δ_D , δ_P , and δ_H directions.

Rotated ellipsoid

The fourth surface fit to the data is similar to the axis-aligned ellipsoid described above, but allows the body to rotate and tilt to obtain a better fit. This procedure adds several parameters to the fitting process, but results in a better overall fit. The quality of fit is still determined as in the Hansen procedure.

Rotated ellipsoid with convex hull center and volume

The fifth surface has the same center coordinates and volume as the convex hull, but attempts to align with the “soluble” data points to minimize distances to its surface. This is an approximation of a circumscribed ellipsoid.

Minimum enclosing ellipsoid

The sixth surface fit is the minimum enclosing ellipsoid for the “soluble” data set. It approximates the smallest volume ellipsoid containing all the “soluble” points. This is not a robust solution to the minimum volume ellipsoid problem, but is instead an approximation using least squares minimization.

Let us now work through an example based on the data set we have already selected and plotted. Assume that all is as we left it in Figure 18. Pointing at the “Fit Surface Bitumen1DataSheet1” item opens another menu titled “Fit surfaces” (Figure 19). At this time all the subheadings in this menu will be light gray. Clicking on “Fit surfaces” starts the surface-fitting portion of the program. As sp3D progresses through the curve-fitting sequence a drop-down box will appear at the top of the sp3D window listing the current surface type being fit. Some fits may require several minutes to complete. When calculations are completed, the program will ask for a location for storing the fit report file (Figure 20). Pick a name and location and click on “Save” to save the report file. A copy of the report will now be displayed using Windows NOTEPAD (Figure 21). This report can now be edited, printed, or copied. The top of the report lists the data set, the report file name, and the number of data points. Each fit type is then listed with its best-fit parameters, including the body center coordinates, the axes lengths if appropriate, the rotation angles (radians) about the x, y, and z axes if appropriate, the body volume, the average radius, the number of outliers, and the Hansen fit parameter. For the convex hull, the center-of-mass, volume, and vertices coordinates and identities are listed. The bottom of the report lists the Hansen number (if any) of each solvent, the solvent description, the solubility parameters of the solvent, the solubility (soluble= 1, insoluble= 0, exact= -1), outlier status (1=outlier) for each of the five ellipsoid fits, and the solvent distance from the body center divided by the body surface distance to the center.

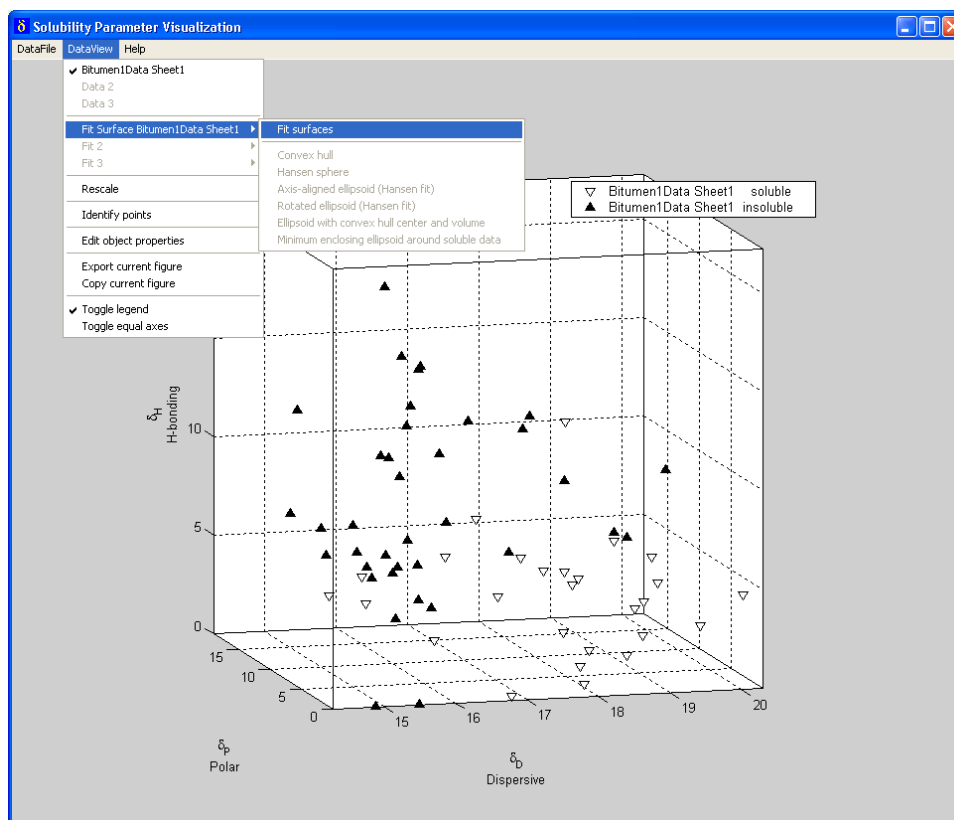


Figure 20. Fit Surfaces Selection Menu

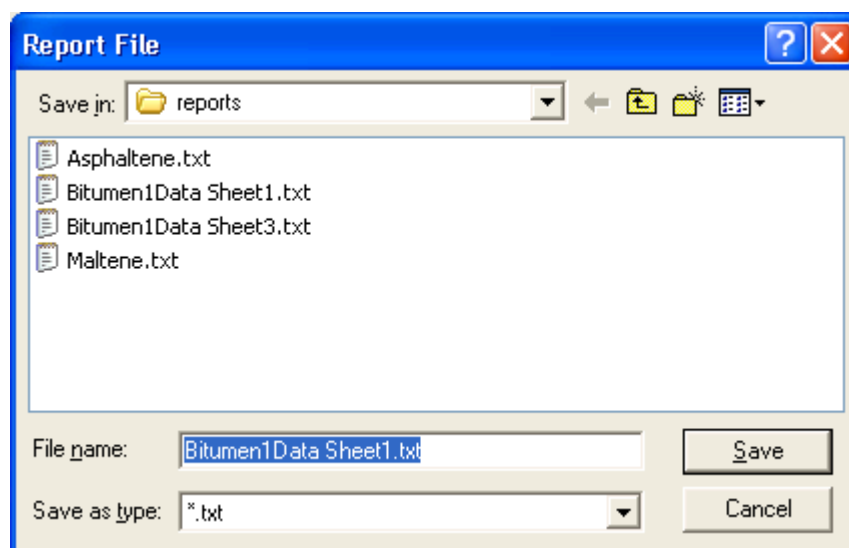


Figure 21. Report File Selection

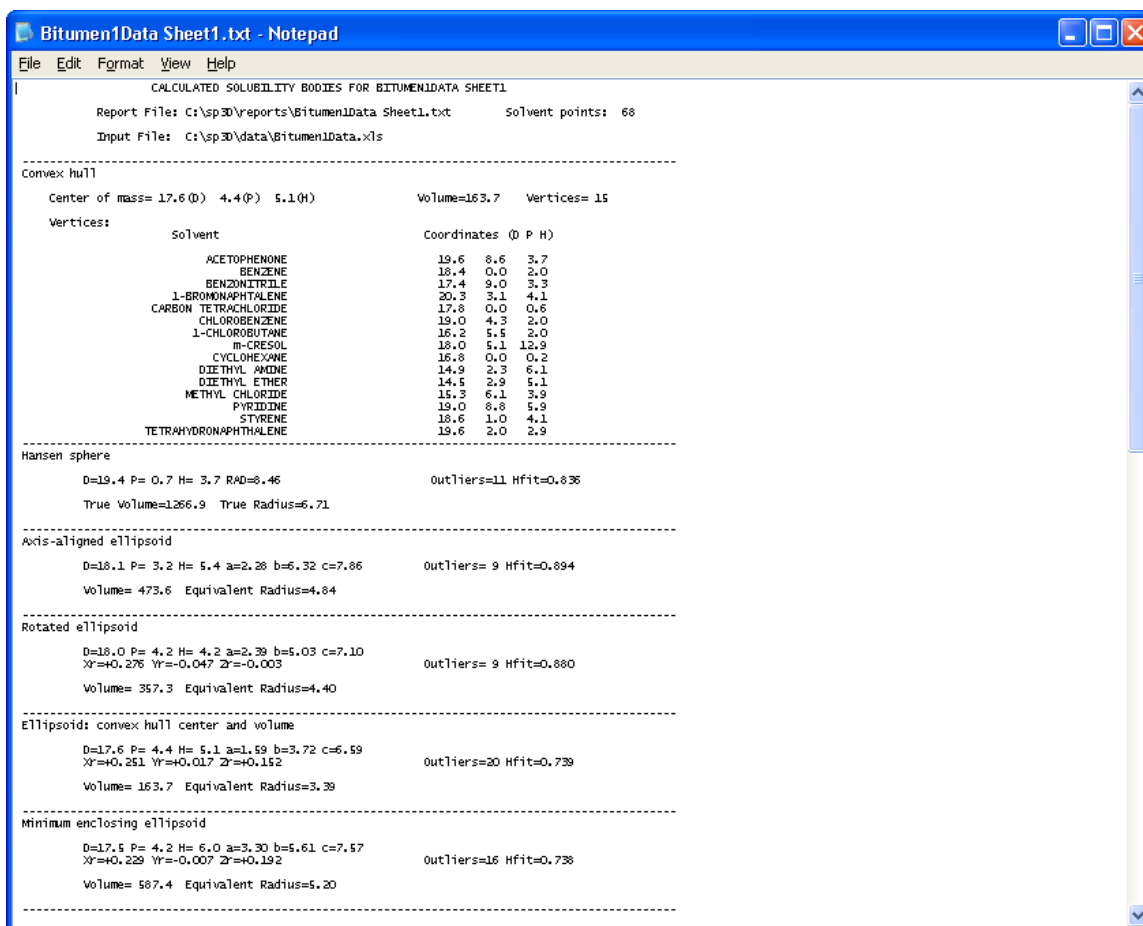


Figure 22. Report of Bitumen1Data Shown in Windows NOTEPAD

By default, the convex hull for the data set is shown when fitting is complete. Any of the fit bodies can now be toggled on and off at any time. The resulting convex hull for this data set is shown in Figure 22 along with the selection menu.

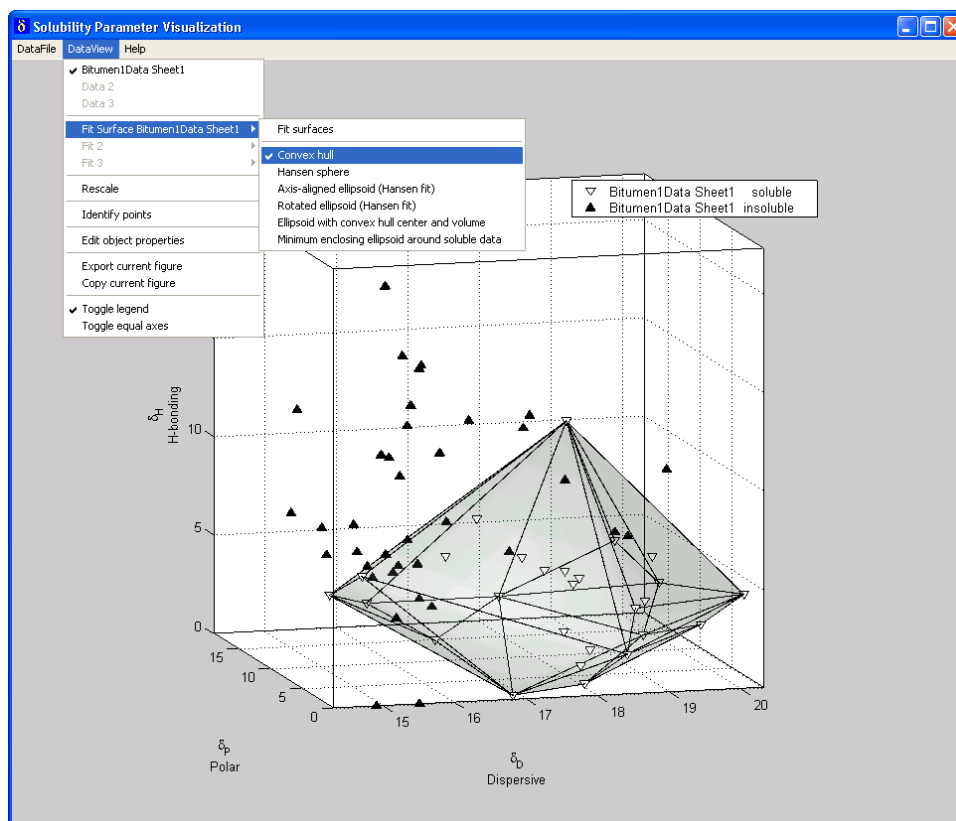


Figure 23. Convex Hull Surface for Bitumen1DataSheet1

At this point many options are available. The figure could be rescaled, the data points could be identified, the data points or the surfaces could be toggled on or off, or another data set could be loaded, fit, and plotted. Another option is to remove this data set from memory by using the “Close” option on the “DataFile” menu.

For this demonstration, we choose to load, fit, and display an additional data set, “aag-1.txt”. Using “Open” on the “DataFile” menu, the data file can be found and the data imported. This, of course, turns on two new lines in the “DataView” menu that allow us to plot the data and fit a surface to the data set. The result is shown in Figure 23 with all the graphics toggled on and set to the Hansen ellipsoid. If we want a more appealing figure, we can rotate the axes to get something like Figure 24.

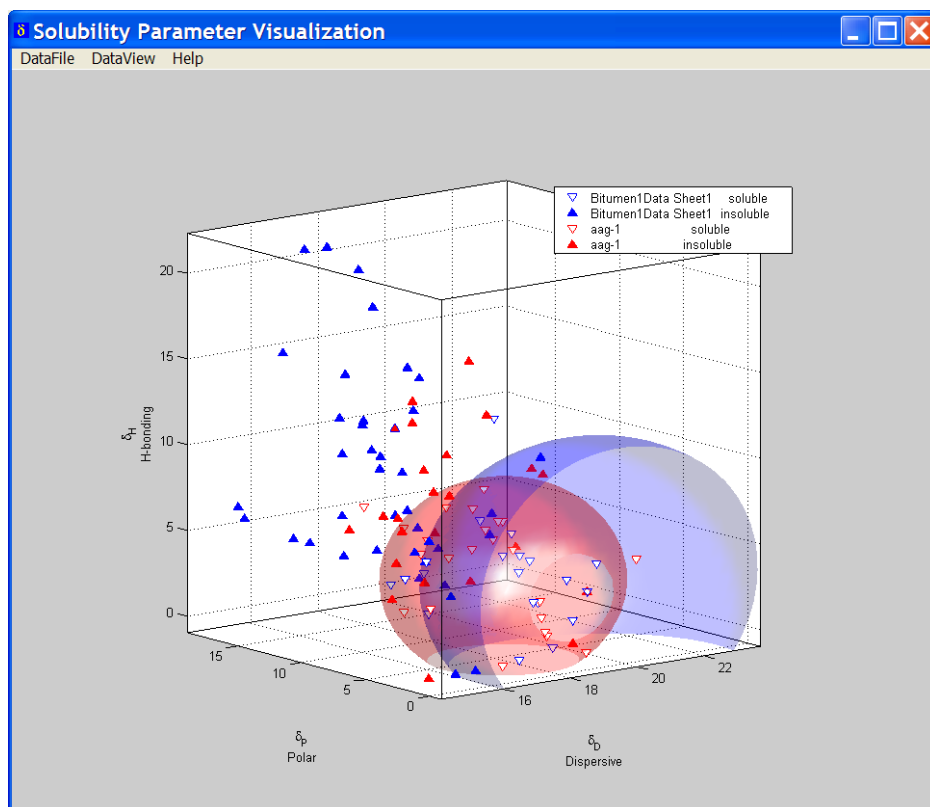


Figure 24. Best Fit Hansen Ellipsoids for Bitumen1DataSheet1 and AAG-1

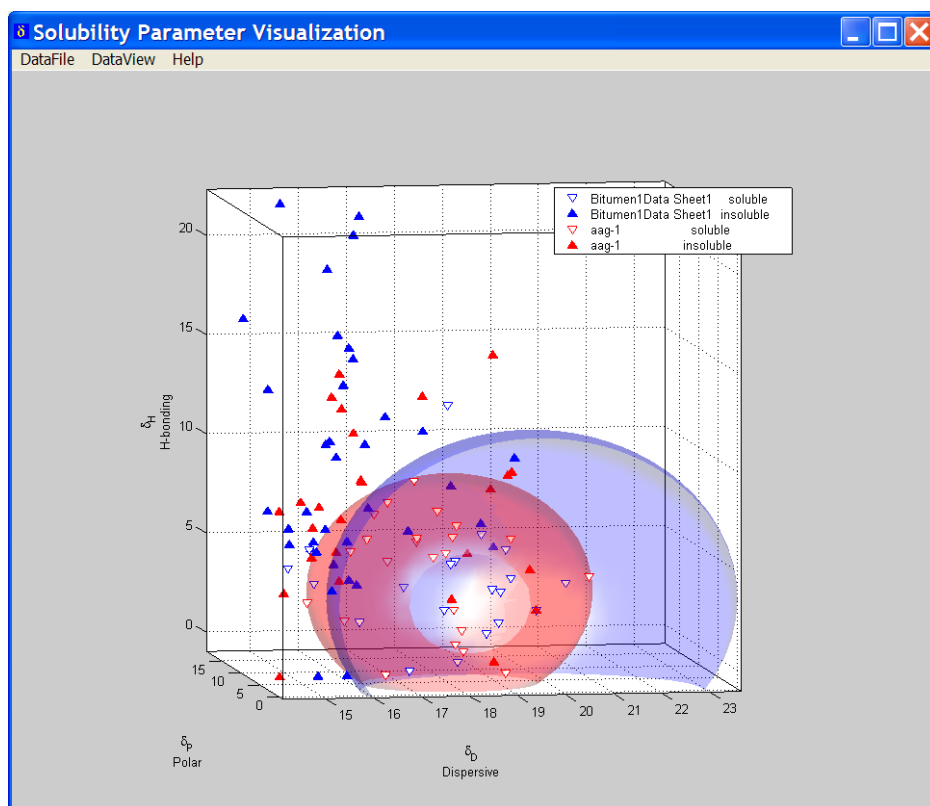


Figure 25. Rotated Hansen Ellipsoids

If we are still not satisfied with the look of the figure, we can change some of the graphics objects' attributes by selecting "Edit object properties" on the "DataView" menu. (Values are not permanently changed; permanent changes are only possible by modifying the sp3D.ini file.) The result of this selection is the appearance of an object selection message as shown in Figure 25. Use the mouse to move the message window out of the way. Do not click on "OK" or the close-window box unless you want to exit this dialog. If we point at one of the blue data points and click the left mouse button, a properties dialog box appears as shown in Figure 26. Using this dialog we can change the shape, size, and color of the data points.

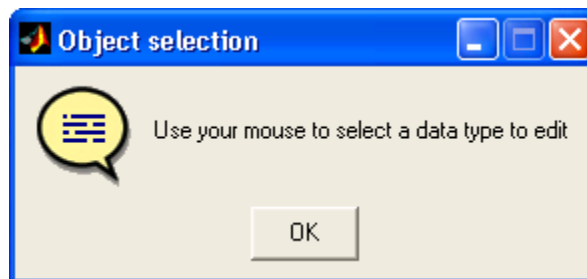


Figure 26. Object Edit Message Window

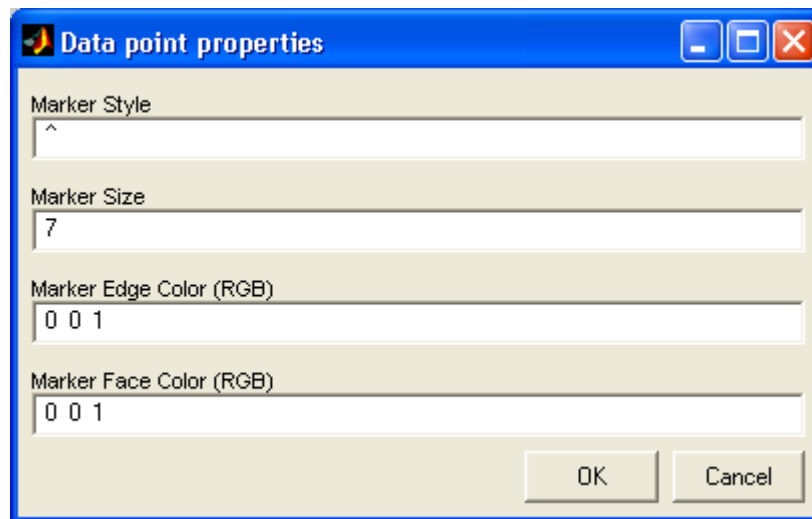


Figure 27. Data Point Properties Dialog

The Appendix contains the codes for interpreting the symbols and colors. If instead we select one of the surfaces, a surface color dialog box like that shown in Figure 27 appears, allowing the color of the surface to be temporarily changed.

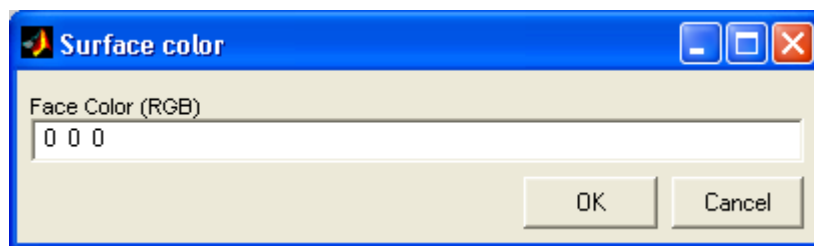


Figure 28. Surface Color Dialog Box

Three other “DataView” menu options have not been discussed in detail. The first of these, “Identify points”, allows the user to select and identify the data points plotted in the solubility space. Clicking on “Identify points” creates a crosshair on the screen that moves when the mouse is moved. When the crosshair is located near the point of interest, click the **right** mouse button. The data point will change size and color, and a drop down list in the upper right corner of the window will display the solvent, its coordinates, and its solubility. Any keyboard key press or a click on the **left** mouse button will end this mode.

Another “DataView” menu option is “Toggle legend”. This selection does just as you would expect it to. It toggles the legend on and off.

The last “DataView” menu option is “Toggle equal axes”. The program scales each axis to fit the edge of the visible cube by default. Clicking on the “Toggle equal axes” option sizes the sides of the cube so that axis increments are the same on all three axes. This shows the user how the true solubility space appears.

Clicking on the “Help” menu provides the user with three further options (Figure 28). These include access to this manual in Adobe “.pdf” format (“Manual”), software/technical support numbers (“Technical support”), and copyright information (“About sp3D”).

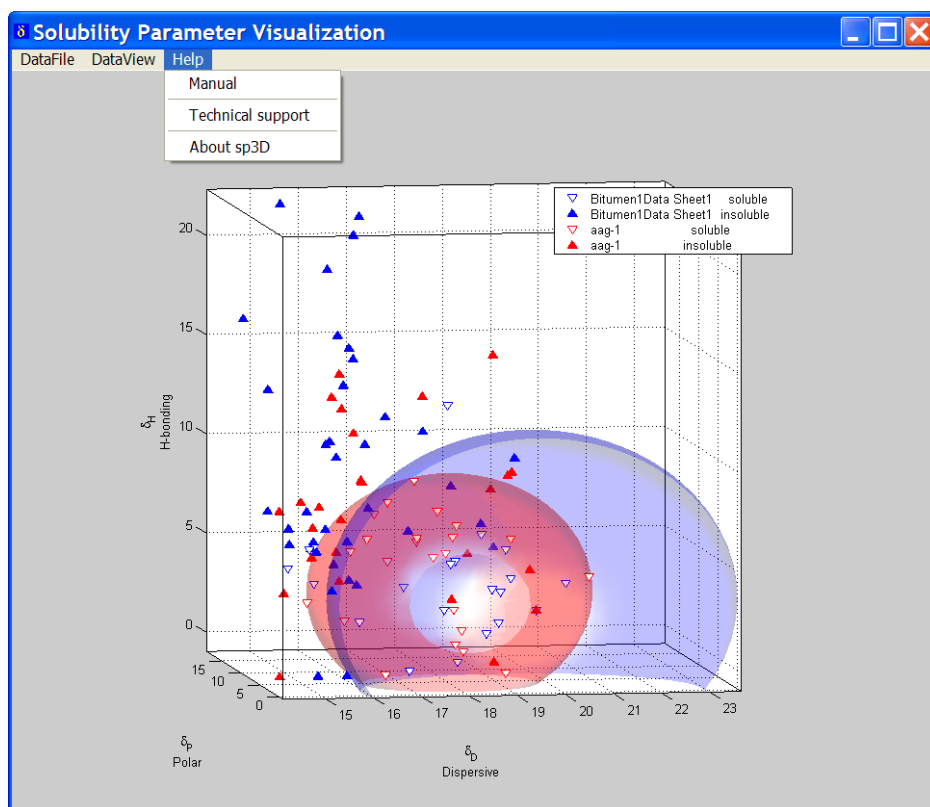


Figure 29. Help Menu Options

DATA FILE CREATION

The simplest way to create a new data file is to edit one of the example files distributed with sp3d and resave the revised file with your new file name. You can edit a *.txt file with a text editor or with Microsoft Excel[®]. The spreadsheet method is easiest and most flexible. Figure 29 shows part of a *.xls data file as viewed in Microsoft Excel[®]. Only the first six columns of the worksheet are used. There should be no header, title, or label line in the worksheet to be accessed by sp3D (the user could easily copy the data from a worksheet with these features to the sp3D-accessible sheet). The “A” column contains a solvent identification number. This could be the Hansen number of the solvent or your own number. It must be an integer, but need not be unique in the column. The “B” column contains the solvent name or description as a character string. An apostrophe may be required if your description begins with a number. Columns “C”, “D”, and “E” contain the dispersive, polar, and hydrogen-bonding solubility coordinates, respectively. These columns should be in numeric format (eg. “xx.x” or “xx.xx”). Column “F” contains a signed integer, indicating solubility. It may be 1, 0, or -1 for soluble, insoluble, or exact, respectively. When the worksheet is complete, it can be saved as an Excel[®] file (*.xls), preferably in the “C:\sp3D\data” directory. If desired, the worksheet can be

| | A | B | C | D | E | F | G |
|----|-----|----------------------|------|------|------|---|---|
| 1 | 5 | ACETIC ACID | 14.5 | 8 | 13.5 | 0 | |
| 2 | 6 | ACETIC ANHYDRIDE | 16 | 11.7 | 10.2 | 0 | |
| 3 | 7 | ACETONE | 15.5 | 10.4 | 7 | 0 | |
| 4 | 10 | ACETONITRILE | 15.3 | 18 | 6.1 | 0 | |
| 5 | 11 | ACETOPHENONE | 19.6 | 8.6 | 3.7 | 1 | |
| 6 | 46 | ANILINE | 19.4 | 5.1 | 10.2 | 0 | |
| 7 | 51 | BENZALDEHYDE | 19.4 | 7.4 | 5.3 | 1 | |
| 8 | 52 | BENZENE | 18.4 | 0 | 2 | 1 | |
| 9 | 55 | BENZONITRILE | 17.4 | 9 | 3.3 | 1 | |
| 10 | 75 | 1-BROMONAPHTALENE | 20.3 | 3.1 | 4.1 | 1 | |
| 11 | 92 | 1-BUTANOL | 16 | 5.7 | 15.8 | 0 | |
| 12 | 102 | n-BUTYL ACETATE | 15.8 | 3.7 | 6.3 | 0 | |
| 13 | 107 | BUTYL LACTATE | 15.8 | 6.5 | 10.2 | 0 | |
| 14 | 115 | GAMMA BUTYROLACTONE | 19 | 16.6 | 7.4 | 0 | |
| 15 | 116 | BUTYRONITRILE | 15.3 | 12.4 | 5.1 | 0 | |
| 16 | 122 | CARBON TETRACHLORIDE | 17.8 | 0 | 0.6 | 1 | |
| 17 | 148 | CHLOROBENZENE | 19 | 4.3 | 2 | 1 | |
| 18 | 152 | 1-CHLOROBUTANE | 16.2 | 5.5 | 2 | 1 | |
| 19 | 156 | CHLOROFORM | 17.8 | 3.1 | 5.7 | 1 | |
| 20 | 169 | m-CRESOL | 18 | 5.1 | 12.9 | 1 | |
| 21 | 181 | CYCLOHEXANE | 16.8 | 0 | 0.2 | 1 | |
| 22 | 182 | CYCLOHEXANOL | 17.4 | 4.1 | 13.5 | 0 | |
| 23 | 183 | CYCLOHEXANONE | 17.8 | 6.3 | 5.1 | 1 | |
| 24 | 184 | CYCLOHEXYLAMINE | 17.2 | 3.1 | 6.5 | 1 | |
| 25 | 209 | DIACETONE ALCOHOL | 15.8 | 8.2 | 10.8 | 0 | |
| 26 | 234 | o-DICHLOROBENZENE | 19.2 | 6.3 | 3.3 | 1 | |
| 27 | 252 | DIETHYL AMINE | 14.9 | 2.3 | 6.1 | 1 | |
| 28 | 255 | DIETHYL ETHER | 14.5 | 2.9 | 5.1 | 1 | |
| 29 | 263 | DIETHYLENE GLYCOL | 16.6 | 12 | 20.7 | 0 | |
| 30 | 272 | DIETHYLENETRIAMINE | 16.7 | 13.3 | 14.3 | 0 | |
| 31 | 273 | DIISOBUTYL KETONE | 16 | 3.7 | 4.1 | 0 | |

Figure 30. Spreadsheet Data File

saved as a tab-delimited text file by selecting “File” in the Excel[®] menu, then “Save as”, and then “Text (Tab delimited) (*.txt)” in the “Save as type:” box. The resulting menu should look like Figure 30. Entering your desired filename and clicking on “Save” will create a tab-delimited text file of your data.

It is possible, although more difficult, to directly create a text data file using a text editor. Tabs should separate the items in each row and each line should end with a carriage return (“Enter” key). The format is shown in Figure 31 where tabs are indicated by the small arrows (→) and the end of each line is shown as a (¶). Only one tab should be used between entries in a line. Save the file as a text (*.txt) file using the “Save as” option on the “File” menu.

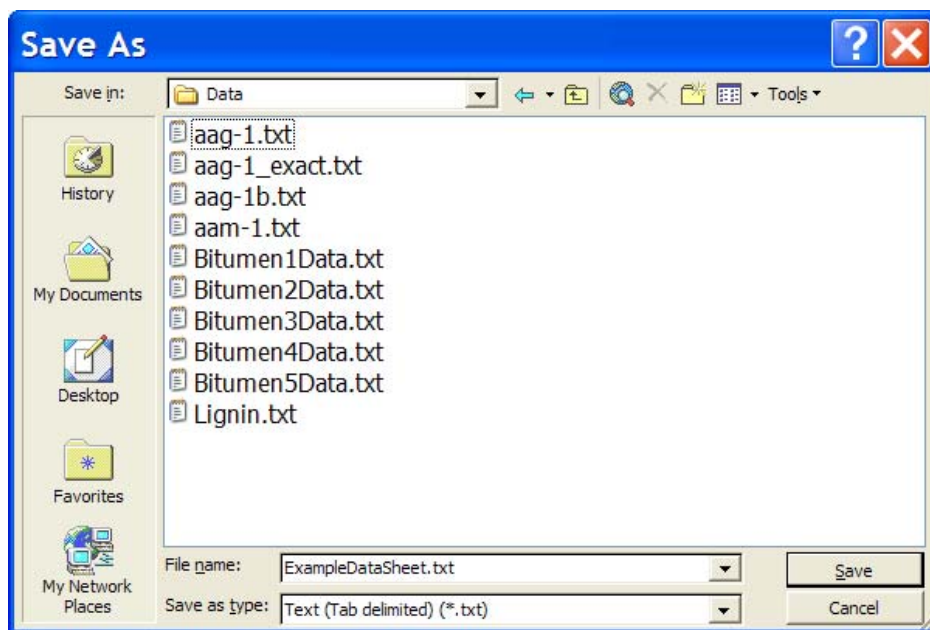


Figure 31. Creating a Tab-Delimited Text File from Excel®

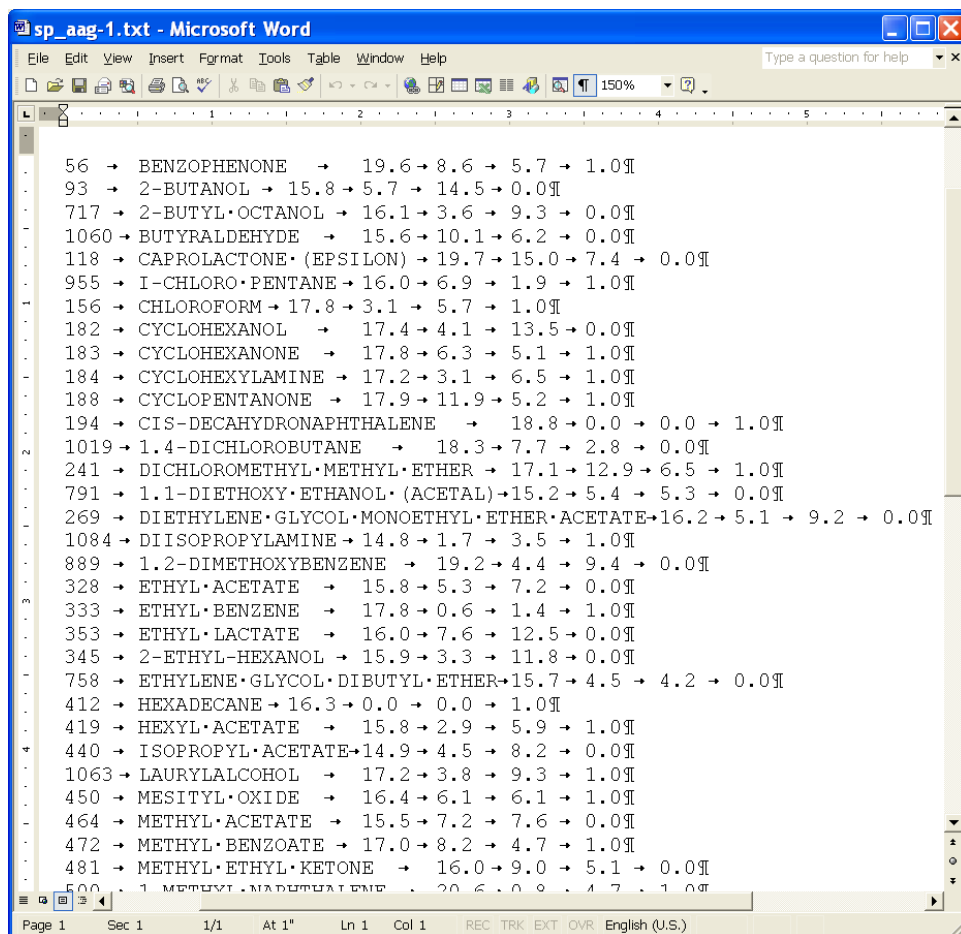


Figure 32. Text File Format in Word®

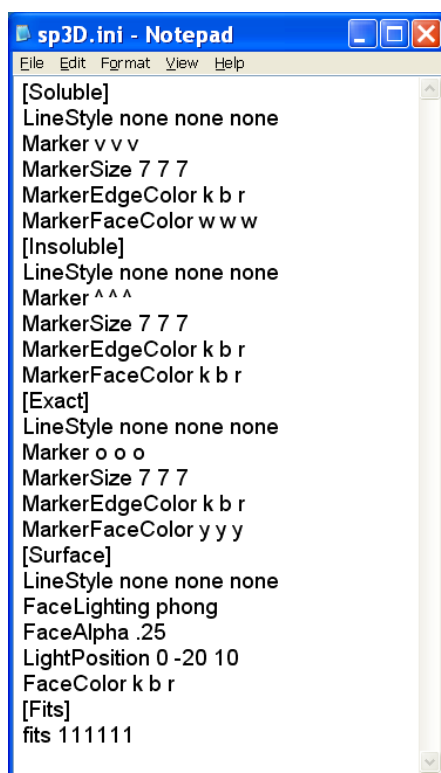
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APPENDIX

Selecting “Preferences” in the “DataFile” menu opens the following window in a text editor (see Figure A1). The entries in this file determine the starting graphic’s settings of sp3D. Six major sections are defined. The “[Soluble]”, “[Insoluble]”, and “[Exact]” sections contain the graphic’s properties of the soluble, insoluble, and exact data points for the three data sets. Refer to Tables A1, A2, and A3 to decode the entries in these sections. Using the “[Insoluble]” section as an example, one can see that for the insoluble points in all three data sets there is no line, the symbols are upward pointing triangles, the symbol sizes are all “7”, and the symbols for data sets 1, 2, and 3 have edge and face colors of black, blue, and red. The “[Surface]” section contains the default attributes of the calculated bodies. “LineStyle” options are described in Table A3. “FaceLighting” options are “flat”, “gouraud”, “phong”, and “none”. These are different algorithms for calculating light reflection. “FaceAlpha” controls the transparency of the body. A value of 1 generates an opaque surface. The “LightPosition” values specify the location of the light source along the dispersive, polar, and h-bonding axes. “FaceColor” defines the default surface colors for the three data sets. In the “[Fits]” section one can select which of the available fits to perform. Computation time can be improved by unselecting those fits that do not prove useful. The six-digit code of ones and zeroes determines which fits are performed. Table A4 lists the fit types by position in the six-digit code. Entering a zero in one of the positions disables the corresponding fit type, with one exception. A zero in the first position will be ignored. The convex hull surface cannot be disabled.



```
sp3D.ini - Notepad
File Edit Format View Help
[Soluble]
LineStyle none none none
Marker v v v
MarkerSize 7 7 7
MarkerEdgeColor k b r
MarkerFaceColor w w w
[Insoluble]
LineStyle none none none
Marker ^ ^ ^
MarkerSize 7 7 7
MarkerEdgeColor k b r
MarkerFaceColor k b r
[Exact]
LineStyle none none none
Marker o o o
MarkerSize 7 7 7
MarkerEdgeColor k b r
MarkerFaceColor y y y
[Surface]
LineStyle none none none
FaceLighting phong
FaceAlpha .25
LightPosition 0 -20 10
FaceColor k b r
[Fits]
fits 111111
```

Figure A1. Default Settings for Preferences

Table A1. Predefined Colors For Symbols And Surfaces*

| RGB Value | Short Name | Long Name |
|-----------|------------|-----------|
| 1 1 0 | y | yellow |
| 1 0 1 | m | magenta |
| 0 1 1 | c | cyan |
| 1 0 0 | r | red |
| 0 1 0 | g | green |
| 0 0 1 | b | blue |
| 1 1 1 | w | white |
| 0 0 0 | k | black |

*Intensities must range from 0 to 1 for RGB (red, green, blue) elements.

Table A2. Data Symbol Types And Definitions

| Symbol Specifier | Description |
|------------------|-------------------------------|
| + | plus sign |
| o | circle |
| * | asterisk |
| . | point |
| x | cross |
| s | square |
| d | diamond |
| ^ | upward pointing triangle |
| v | downward pointing triangle |
| > | right pointing triangle |
| < | left pointing triangle |
| p | five-pointed star (pentagram) |
| h | six-pointed star (hexagram) |
| None | no symbol |

Table A3. Line Styles

| Symbol | Line Style |
|--------|-------------|
| - | solid line |
| -- | dashed line |
| : | dotted line |
| -. | dash-dot |

| | |
|------|---------|
| | line |
| none | no line |

Table A4. Position Code for Fit Types

| Position | Fit type |
|-----------------|--|
| 1 | convex hull |
| 2 | Hansen ellipsoid |
| 3 | axis-aligned ellipsoid |
| 4 | rotated ellipsoid |
| 5 | rotated ellipsoid with convex hull center and volume |
| 6 | minimum enclosing ellipsoid |
| | |
| Example | Fit types |
| 111111 | all fits are performed |
| 111101 | all fits are performed except number 5 |
| 110100 | fits 1, 2, and 4 are performed |
| 010100 | fits 1, 2, and 4 are performed (convex hull fit is always performed) |
| | |