New Procedure To Calculate the Hansen Solubility Parameters of Polymers

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ABSTRACT: The simplest experimental method to determine the Hansen solubility parameters (HSPs) for a polymer is to evaluate whether or not it dissolves in selected solvents. Those solvents dissolving the polymer will have HSPs closer to those of the polymer than those that do not. A computer program or graphical method can then be used to find the HSP for the polymer. In this work, an improved method for calculating the HSP of polymers, based on the Nelder–Mead optimization algorithm, is presented. The results of this program fit the data very well. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 31–36, 2007

Key words: adhesion; coatings; cohesion

INTRODUCTION

Solubility parameters have found their greatest use in the coatings industry, aiding in the selection of solvents. They are used in other industries, however, to predict the compatibility of polymers, chemical resistance, and permeation rates and even to characterize the surfaces of pigments, fibers, and fillers. Liquids with similar solubility parameters will be miscible, and polymers will dissolve in solvents whose solubility parameters are not too different from their own.[1]

The solubility parameter has been used for many years to select solvents for coating materials. A lack of total success has stimulated research. The skill with which solvents can be optimally selected with respect to the cost, solvency, workplace environment, external environment, evaporation rate, flash point, and so forth has improved over the years as a result of a series of improvements in the solubility parameter concept and widespread use of computer techniques. Most, if not all, commercial suppliers of solvents have computer programs to help with solvent selection.

The term *solubility parameter* was first used by Hildebrand and Scott.[2,3] The earlier work of Scatchard[4] and others was contributory to this development. The Hildebrand solubility parameter (δ) is defined as the square root of the cohesive energy density:

$$\delta = \sqrt{\frac{E}{V}} \qquad (1)$$

where V is the molar volume of the pure solvent and E is its (measurable) energy of vaporization. δ is an important quantity for predicting solubility relations, as can be seen in the following brief introduction. Thermodynamics requires that the free energy of mixing (ΔG^M) be zero or negative for the solution process to occur spontaneously. The free energy change for the solution process is given by the following relation:

$$\Delta G^M = \Delta H^M - T\Delta S^M \qquad (2)$$

where ΔH^M is the heat of mixing, T is the absolute temperature, and ΔS^M is the entropy change in the mixing process.

Equation (3) gives ΔH^M as proposed by Hildebrand and Scott:[2,3]

$$\Delta H^M = \varphi_1 \varphi_2 V_M (\delta_1 - \delta_2)^2 \qquad (3)$$

where subscript 1 and 2 are related to solute and solvent, respectively. The φ variables are volume fractions of the solvent and polymer, and V_M is the volume of the mixture.

Equation (3) is not correct. This equation has often been cited as a shortcoming of this theory, in that only positive heats of mixing are allowed. It has been shown by Patterson and coworkers[5–10] that the noncombinatorial free energy of solution ($\Delta G^M_{noncomb}$), not ΔG^M, is given by the right-hand side of eq. (3). The correct relation is

$$\Delta G^M_{noncomb} = \varphi_1 \varphi_2 V_M (\delta_1 - \delta_2) \qquad (4)$$

$\Delta G^M_{noncomb}$ includes all free energy effects other than the combinatorial entropy of solution occurring because

of simple mixing of the components. Equation (4) is consistent with the Prigogine corresponding states theory of polymer solutions and can be differentiated to give expressions predicting both positive and negative heats of mixing.[3,5] Therefore, both positive and negative heats of mixing can be expected from theoretical considerations and have been measured accordingly. It has been clearly shown that solubility parameters can be used to predict both positive and negative heats of mixing. Previous objections to the effect that only positive values are allowed in this theory are not correct.

A more detailed description of the theory presented by Hildebrand and the succession of research reports that have attempted to improve on it can be found in Barton's extensive handbooks.[11,12] The slightly older but excellent contribution of Gardon and Teas[13] is also a good source of related information, particularly for coatings and adhesion phenomena. The approach of Burrell,[14] who divided solvents into hydrogen-bonding classes, has found numerous practical applications; the approach of Blanks and Prausnitz[15] divides the solubility parameter into two components, nonpolar and polar. Both are worthy of mention.

A widely used solubility parameter approach to predicting polymer solubility is that proposed by the Hansen. The basis of these so-called Hansen solubility parameters (HSPs) is that the total energy of vaporization of a liquid consists of several individual parts.[16–19] These arise from (atomic) dispersion forces, (molecular) permanent-dipole/permanent-dipole forces, and (molecular) hydrogen bonding (electron exchange). The basic equation that governs the assignment of Hansen parameters is that the total cohesion energy (E) must be the sum of the individual energies that make it up:

$$E = E_D + E_P + E_H \qquad (5)$$

where E_D, E_P, and E_H are dispersion, permanent-dipole/permanent-dipole, and hydrogen bonding forces, respectively. Dividing this by the molar volume gives the square of the total (or Hildebrand) solubility parameter as the sum of the squares of the Hansen D, P, and H components:

$$E/V = E_D/V + E_P/V + E_H/V \qquad (6)$$

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (7)$$

where δ_d, δ_p, and δ_h are the dispersion, polar, and hydrogen-bond parts of HSPs, respectively. To sum up this section, we emphasize that HSPs quantitatively account for the cohesion energy (density). An experimental latent heat of vaporization has been considered much more reliable as a method for arriving at a cohesion energy than using molecular orbital calculations or other calculations based on potential functions. Indeed, the goal of such extensive calculations for polar and hydrogen-bonding molecules should be to accurately arrive at the energy of vaporization.

In this work, we focused on Hansen's algorithm and program to calculate HSPs of polymers, and we succeeded in improving this algorithm and omitting the numerical errors of Hansen's numerical method.

RESULTS

The algorithm of our work is the same as Hansen's algorithm for calculating HSPs for polymers.[1] The data input is by the solvent number followed by an indication of the quality of the interaction with that solvent. 1 indicates a good solvent, whereas 0 is used for a bad solvent. What is considered good or bad varies according to the level of the interaction being studied. This can be a solution or not, a given percentage of swelling or uptake, a breakthrough time less than a given interval, permeation coefficients higher than a given value, long-time suspension of a pigment, and so forth. The program systematically evaluates the input data with a quality-of-fit function called the *Desirability Function*.[20] This suggestion was made by a reputed statistician many years ago as the most appropriate statistical treatment for this type of problem. It has been in use since the late 1960s. The function has the following form:

$$\text{DataFit} = (A_1 \times A_2 \times \cdots \times A_n)^{1/n} \qquad (8)$$

where n is the number of solvents for which there are experimental data in the correlation. DataFit in eq. (8) approaches 1.0 as the fit improves during an optimization and reaches 1.0 when all the good solvents are included within the sphere and all the bad ones are outside of it:

$$A_i = e^{(\text{ErrorDistance})} \qquad (9)$$

A_i for a given good solvent within the sphere and for a given bad solvent outside the sphere is 1.0. The error distance is the distance to the sphere boundary for the solvent in error either as being good and outside the sphere or as being bad and inside the sphere. R_o is the radius of the sphere, and R_a is the distance from a given solvent point to the center of the sphere. R_o is one of the targets of our program that is calculated. R_a is calculated with eq. (10):

$$R_a = \sqrt{4(\delta_d - \delta_{dp})^2 + (\delta_p - \delta_{pp})^2 + (\delta_h - \delta_{hp})^2} \qquad (10)$$

where δ_d, δ_p, and δ_h are the HSPs of the solvent and δ_{dp}, δ_{pp} and δ_{hp} are the HSPs of the polymer, which are targets of our program with R_o. These four target parameters are calculated from our algorithm as illustrated in Figure 1.
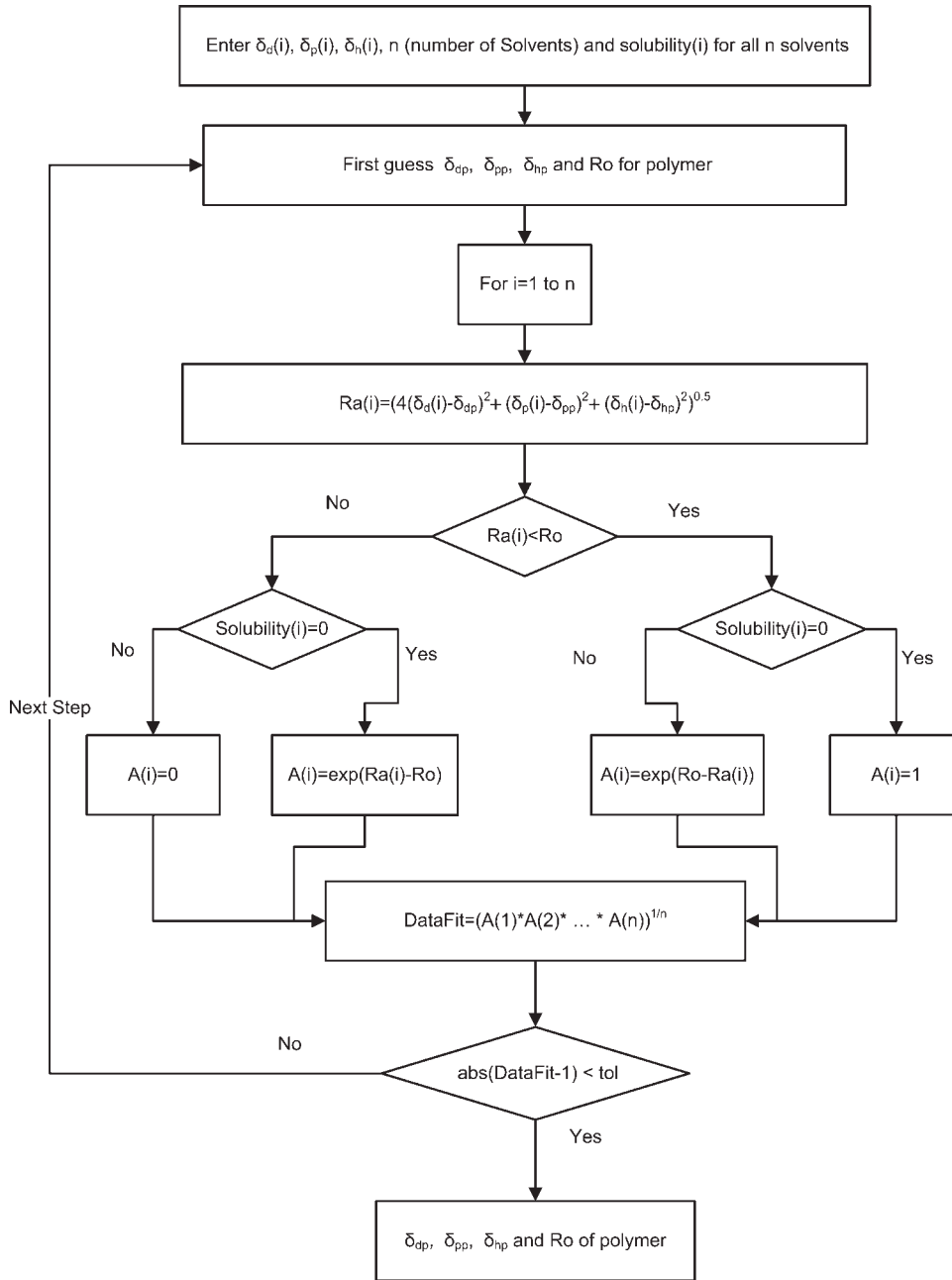
Figure 1 Flowchart of the program.

If R_a for a solvent is smaller than R_o of the polymer, this solvent can dissolve the polymer ($R_a/R_o < 1$), and if the R_a for a solvent is larger than R_o of the polymer, this solvent cannot dissolve the polymer ($R_a/R_o > 1$). The equality of R_a with R_o is the boundary of solubility and nonsolubility. For a good solvent outside the sphere, an error enters DataFit according to

$$A_i = e^{+(R_o - R_a)} \tag{11}$$

Such errors are often found for solvents having low molecular volumes. For a bad solvent inside the sphere, the contribution to the DataFit is

$$A_i = e^{+(R_a - R_o)} \tag{12}$$

Such errors can sometimes be found for larger molecular species such as plasticizers. This is not unexpected for the reasons mentioned earlier.

This program assumes a starting point based on an average of HSPs for all solvents. In this section, our method changes from the method of Hansen for the calculation of the polymer HSP. Hansen performed his calculation with a pseudo-optimization method, and his results for DataFit are not equal to 1.0 for many examples. In this work, we applied the Nelder–Mead algorithm, which was presented by Lagarias

et al.[21] and is available in the Optimization Toolbox of MATLAB, to minimize the objective function. We defined the objective function for this optimization process as follows:

$$\text{ObjectiveFunction} = |\text{DataFit} - 1| \qquad (13)$$

Our aim in this study was finding the global minimum of this objective function. The aim of this algorithm is the calculation of R_o value for the polymer, for which all good solvents have R_a values smaller than this R_o value and all bad solvents have R_a values larger than this R_o value. After testing the program for several polymers, we found that the value of DataFit in eq. (8) is a very important factor for calculating the

HSP of the polymer (see Fig. 1). Hansen's program finds the HSP of the polymer in the neighborhood of the answer region, and in this program, Hansen did not recommend that DataFit must be unity. This latter condition influences the calculated values of the polymer HSP and radius of the solubility sphere very much. For more illustration of our explanation, we can refer to the example of poly(ether sulfone), which was illustrated by Hansen.[1] This example is very useful for illustrating some problems of Hansen's program for calculating the HSPs of polymers. Hansen tested 41 solvents for this polymer, and the results are in Table I. In this work, Hansen obtained the value of 0.999 for DataFit and the values of 19.6, 10.8, 9.2, and 6.2 for δ_d, δ_p, δ_h, and R_o, respectively, in this problem.

TABLE I
Results for a Sample of Poly(ether sulfone) Compared with Hansen's Results

Solvent	δ_d	δ_p	δ_h	Solubility	R_a/R_o[a]	R_a/R_o[b]
Methyl-2-pyrrolidone	18	12.3	7.2	1	0.655	0.7576
Dimethyl formamide	17.4	13.7	11.3	1	0.915	0.9575
Acetophenone	19.6	8.6	3.7	1	0.955	0.9365
Methylene dichloride	18.2	6.3	6.1	1	0.99	0.9998
Dimethyl sulfoxide	18.4	16.4	10.2	0	0.996	1
γ-Butyrolactone	19	16.6	7.4	1	0.998	1
Ethylene dichloride	19	7.4	4.1	0	1.007	1.0002
Isophorone	16.6	8.2	7.4	0	1.094	1.147
o-Dichlorobenzene	19.2	6.3	3.3	0	1.204	1.1653
Tetrahydrofuran	16.8	5.7	8	0	1.237	1.2464
Diacetone alcohol	15.8	8.2	10.8	0	1.321	1.3403
Methyl ethyl ketone	16	9	5.1	0	1.368	1.4091
Acetone	15.5	10.4	7	0	1.371	1.4199
2-Nitropropane	16.2	12.1	4.1	0	1.387	1.433
Ethylene glycol monoethyl ether	16.2	9.2	14.3	0	1.395	1.3722
Propylene carbonate	20	18	4.1	0	1.429	1.3669
Cyclohexanol	17.4	4.1	13.5	0	1.467	1.389
Chloroform	17.8	3.1	5.7	0	1.483	1.4333
Trichloroethylene	18	3.1	5.3	0	1.485	1.4314
1,4-Dioxane	19	1.8	7.4	0	1.493	1.3923
Ethyl acetate	15.8	5.3	7.2	0	1.547	1.5449
Ethylene glycol monobutyl ether	16	5.1	12.3	0	1.563	1.5253
Chlorobenzene	19	4.3	2	0	1.576	1.5049
Nitroethane	16	15.5	4.5	0	1.58	1.6061
Ethylene glycol monomethyl ether	16.2	9.2	16.4	0	1.618	1.556
Butyl acetate	15.8	3.7	6.3	0	1.741	1.7129
1-Butanol	16	5.7	15.8	0	1.777	1.6978
Methyl isobutyl ketone	15.3	6.1	4.1	0	1.782	1.7758
Nitromethane	15.8	18.8	5.1	0	1.899	1.8855
Toluene	18	1.4	2	0	1.978	1.8834
Ethanol	15.8	8.8	19.4	0	2.077	1.9616
Diethylene glycol	16.6	12	20.7	0	2.101	1.9665
Benzene	18.4	0	2	0	2.129	2.0073
Diethyl ether	14.5	2.9	5.1	0	2.183	2.1305
Ethanol amine	17	15.5	21.2	0	2.241	2.0905
Carbon tetrachloride	17.8	0	0.6	0	2.301	2.1805
Propylene glycol	16.8	9.4	23.3	0	2.457	2.2741
Methanol	15.1	12.3	22.3	0	2.575	2.4211
Hexane	14.9	0	0	0	2.745	2.6315
Ethylene glycol	17	11	26	0	2.837	2.614
Formamide	17.2	26.2	19	0	3.044	2.8435

[a] Obtained with Hansen's program ($\delta_d = 19.6$, $\delta_p = 10.8$, $\delta_h = 9.2$, $R_o = 6.2$, DataFit $= 0.999$).[1]
[b] Obtained with our program ($\delta_d = 20.0902$, $\delta_p = 10.6302$, $\delta_h = 9.5715$, $R_o = 6.7162$, DataFit $= 1$).

These results were repeated with our method with the value of 0.999 for DataFit. The obtained results of our program with the value of 1 for DataFit, as shown in Table I, are 20.0902, 10.6302, 9.5715, and 6.7162 for δ_d, δ_p, δ_h, and R_o, respectively. These values are different from Hansen's values!

Our program contains three functions. This program was written with the MATLAB software base and is shown in the appendix. The main function is the HSP.m function. This function works as illustrated in Figure 1. The function after running, called the Solvent_Database.m function, contains the solvent properties needed for calculation. After the definition of the parameters, it needs values for the first guess of target parameters δ_{dp}, δ_{pp}, δ_{hp}, and R_o. In this program, we used the average values of δ_d, δ_p, and δ_h of the solvents for the first guess of δ_{dp}, δ_{pp}, and δ_{hp} and the sum of the square root of the first guess of δ_{dp}, δ_{pp}, and δ_{hp} for the first guess of R_o. After this section, the QF.m function is called by the fminsearch function of MATLAB. The QF.m function contains the DataFit function. Fminsearch is one of the interior functions of MATLAB. This function works with the Nelder–Mead algorithm to minimize a function. In this section, we want to minimize the objective function of eq. (13). After the QF.m is minimized, the results, containing δ_{dp}, δ_{pp}, δ_{hp}, and R_o of the polymer and the solvent properties, are shown in the workspace.

As illustrated in Table I, the values of HSP for poly (ether sulfone) are very much affected by the value of DataFit. The difference between the values of DataFit in Hansen's work and our work is 0.001, but this small difference affects the value of the polymer HSP considerably. This uncertainty in the HSP values for poly (ether sulfone) affects the values of HSP and R_o of the polymer. One of the most important of these effects is the prediction of the solubility of poly(ether sulfone) in dimethyl sulfoxide (see Table I). Hansen's program predicts that poly(ether sulfone) will be soluble in dimethyl sulfoxide, but he showed that this is not true experimentally. Our program predicts that dimethyl sulfoxide will not be a solvent for poly(ether sulfone). If the value of DataFit goes far from unity, the uncertainty of the prediction is increased.

CONCLUSIONS

The method presented in this article determines more accurately the HSP and radius of the interaction sphere of a polymer because of the original work of Hansen[1] with an improved mathematical method.

This program is presented in this article, is simple, and can be easily implemented on a computer. DataFit is one of the most important parameters in the calculation of the polymer HSP. A small deviation of DataFit from unity causes a quite large deviation in the values of the HSP and radius of the interaction sphere of the polymer. A deviation in the values of HSP and R_o of the polymer causes error in the prediction of the solubility of the polymer in solvents.

This method omits the numerical errors of Hansen's method for determining the HSP of a polymer.

APPENDIX

For performing this program, please insert these three functions into a directory, then insert this directory as the directory of MATLAB workspace, then type HSP in the workspace and see results.

HSP.m

```
% A Simple Program To Calculate Hansen Solubility
    Parameters
% Farhad Gharagheizi & Mahmood Torabi Angaji,
% Department of Chemical Engineering,
% Faculty of Engineering, University of Tehran.
% 30 September, 2005.
%-----------------------------------------------------------
clc
clear all
Solvents_Database;
delta_d=(data(:,1))';
delta_p=(data(:,2))';
delta_h=(data(:,3))';
solubility=(data(:,4))';
a(1)=mean(delta_d);
a(2)=mean(delta_p);
a(3)=mean(delta_h);
a(4)=sqrt(a(1)^2+a(2)^2+a(3)^2);
guess=a;
options=optimset('Display','off');
res=1;
while res>1e-4;
[delta res]=fminsearch(@QF,guess,options,delta_d,
    delta_p,delta_h,.
solubility,n);
guess=delta;
end
d_d=delta(1); d_p=delta(2); d_h=delta(3); R_o=delta(4);
R_a=sqrt(4*(d_d-delta_d).^2 + (d_p-delta_p).^2 +
    (d_h-delta_h).^2);
RED=(R_a/R_o);
clc
disp('****************************************************')
disp('Delta_d Delta_p Delta_h Solub RED')
disp('****************************************************')
disp([delta_d' delta_p' delta_h' solubility' RED'])
disp('Data Fit ==')
Data_Fit=1+QF(delta,delta_d,delta_p,delta_h,
    solubility,n);
disp(Data_Fit)
```

```
disp('Delta_d Delta_p Delta_h R_o')
disp([d_d d_p d_h R_o])
```

QF.m

```
function y=QF(x,delta_d,delta_p,delta_h,solubility,n)
d_d=x(1);
d_p=x(2);
d_h=x(3);
R_o=x(4);
R_a=sqrt(4*(d_d-delta_d).^2 + (d_p-delta_p).^2 +
   (d_h-delta_h).^2);
for i=1:n,
    if R_a(i)>R_o;
       if solubility(i)==0;
          A(i)=1;
       else
          A(i)=exp(R_o-R_a(i));
       end
    else R_a(i)<R_o;
       if solubility(i)==0;
          A(i)=exp(R_a(i)-R_o);
       else
          A(i)=1;
       end
    end
end
y=abs(((prod(A))^(1/n))−1);
```

Solvent_Database.m

```
%Numbr of Solvents n=41;
```

% delt_d	delta_p	delta_h	Solub
18.0	12.3	7.2	1.0;
17.4	13.7	11.3	1.0;
19.6	8.6	3.7	1.0;
18.2	6.3	6.1	1.0;
18.4	16.4	10.2	0;
19.0	16.6	7.4	1.0;
19.0	7.4	4.1	0;
16.6	8.2	7.4	0;
19.2	6.3	3.3	0;
16.8	5.7	8.0	0;
15.8	8.2	10.8	0;
16.0	9.0	5.1	0;
15.5	10.4	7.0	0;
16.2	12.1	4.1	0;
16.2	9.2	14.3	0;
20.0	18.0	4.1	0;
17.4	4.1	13.5	0;
17.8	3.1	5.7	0;
18.0	3.1	5.3	0;
19.0	1.8	7.4	0;
15.8	5.3	7.2	0;
16.0	5.1	12.3	0;
19.0	4.3	2.0	0;
16.0	15.5	4.5	0;
16.2	9.2	16.4	0;
15.8	3.7	6.3	0;
16.0	5.7	15.8	0;
15.3	6.1	4.1	0;
15.8	18.8	5.1	0;
18.0	1.4	2.0	0;
15.8	8.8	19.4	0;
16.6	12.0	20.7	0;
18.4	0	2.0	0;
14.5	2.9	5.1	0;
17.0	15.5	21.2	0;
17.8	0	0.6	0;
16.8	9.4	23.3	0;
15.1	12.3	22.3	0;
14.9	0	0	0;
17.0	11.0	26.0	0;
17.2	26.2	19.0	0

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