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Effect of Calculation Method on Values of Hansen Solubility Parameters of Polymers

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Summary

The simplest experimental method to determine the Hansen Solubility Parameters (HSP) for a polymer is to evaluate whether or not it dissolves in selected solvents. The solvents dissolve the polymer have HSP closer to it than those which don't. Then a computer program can be used to find the HSP of the selected polymer. In this work, the effect of calculation method on the values of HSP has been analyzed completely. The results show that optimization method for calculation of HSP is an important factor in the precision of obtained values of these parameters.

Introduction

A solution may be defined as a mixture of two or more substances which has uniform chemical and physical properties throughout. The purpose of using solvents is to convert substances into a form suitable for a particular use. Some of the uses of solvents are in adhesives, coatings, electronics, pharmaceutical, etc. Solvents vary in their dissolving power. So there should be a criterion helps to select proper solvents for certain uses. Here come solubility parameters.

Solubility parameters provide a simple method of predicting and calculating the adhesive and cohesive properties of materials, particularly for polymers. Knowing solubility parameters is necessary for studying polymer dissolution and polymer processing methods such as: blending, coating, casting, etc, and predicting polymer-polymer, polymer-solvent, random copolymer, and multi-component equilibria.

Solubility parameter was developed by Hildebrand and Scott [1-3] who assumed that the mutual solubility of components depends on the cohesive pressure, *c*. The square root of cohesive pressure is the Hildebrand's solubility parameter, δ:

$$\delta = \sqrt{c} = \sqrt{\frac{\Delta H_{\mathrm{v}} - RT}{V_m}} \tag{1}$$

where ΔH_{v} is heat of vaporization, R is gas constant, T is absolute temperature, and V_m is molar volume of solvent. Frequently the term RT is neglected because it accounts for only 5-10% of the heat of vaporization. The Hildebrand model takes into account only the dimension of molecular segments participating in the process of solvation and dispersion interactions. Therefore, the model is useful to predict the solubility of nonpolar substrates. The solubility parameter of solvent and solute are compared and if they are similar, there is high probability that the solute is soluble in the solvent. This model is an experimental and mathematical development of the simple rule of "like dissolves like".

Solvents and solutes also interact by electron pair, donor-acceptor, and hydrogen bonding interactions. So the above Hildebrand's model is not fully applicable, especially when solvents and solutes may apply these interactions in the solubilizing process. Arkel [4], Small [5], and Anderson [6], Prausnitz and co-workers [7-10] divided the total solubility parameter into two main components: δ_λ the nonpolar, and δ_τ the polar solubility parameter which are related to the Hildebrand parameter by:

$$\delta^2 = \delta_\lambda^2 + \delta_\tau^2 \qquad (2)$$

Hansen proposed a practical extension of Hildebrand parameter method to polar and hydrogen bonding systems. It was assumed that dispersion, polar and hydrogen bonding parameters were valid simultaneously. So Hansen defined solubility parameters by the following equation:

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (3)$$

where δ_t is Hansen's total solubility parameter, δ_d the dispersive term, δ_p the polar term, and δ_h the hydrogen bonding term [11-14].

Hansen defined solvents as points in tree-dimensional space and solutes as volumes (or spheres of solubility) like Fig (1). If a solvent point is within the boundaries of a solute volume space, then the solute can be dissolved by the solvent. If the solvent point is placed outside the solubility sphere, such a solvent does not dissolve the solute [15].

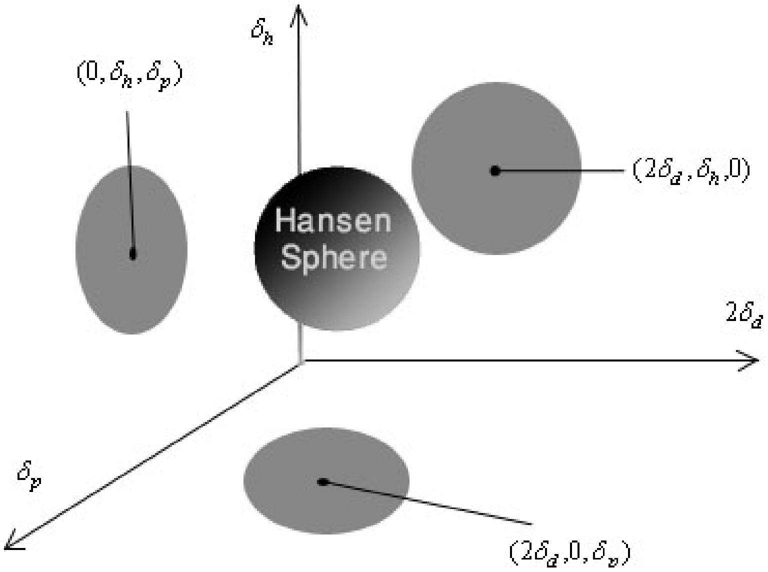

Figure 1 – Hansen Sphere in the Schematic form.

In this work, we focused on the Hansen's algorithm to calculate HSP and successfully, it was improved and the numerical errors of Hansen's calculation method was omitted to obtain more precise values for solubility parameters.

Method and results

The algorithm of our program is same as the Hansen's one to calculate HSP. The program uses input data based on quality of interactions between polymer and solvent. It means using '1' for good solvents, while '0' for bad solvents. The program evaluates input data using a quality of fit function called "Desirability function" [16]. This function made by a reputed statistician as a most statistical treatment for this kind of problems. The function has following form:

$$DataFit = F = \sqrt[n]{\prod_{i=1}^{n} f_i} \qquad (4)$$

where n is the number of solvents tested in dissolving experiment.

During the optimization process, F comes near 1.0 as fit improves, and becomes 1.0 when all the good solvents are placed within the solubility sphere of solute and all the bad solvents are outside of it.

f_i in Eq (4) is defined by:

$$f_i = e^{-(Error\ Distance)} \qquad (5)$$

f_i for a given good solvent within the sphere and for a given bad solvent outside the sphere is 1.0. There is an error if a good solvent is outside or a bad solvent is inside the sphere. So the distance between sphere boundary and solvent point is named *error distance*.

R_o, is the radius of the sphere which must be calculated. R_a, is the distance between given solvent point and the center of the sphere which is calculated by this equation:

$$R_a = \sqrt{4(\delta_d - \delta_{dp})^2 + (\delta_p - \delta_{pp})^2 + (\delta_h - \delta_{hp})^2} \qquad (6)$$

where δ_d, δ_p, and δ_h, are HSP of solvent and δ_{dp}, δ_{pp}, and δ_{hp}, are HSP of polymer which we want to calculate them.

For a good solvent outside the sphere, an error enters the F by:

$$f_i = e^{+(R_o - R_{ai})} \qquad (7)$$

Such errors are often found for solvents with low molecular volume.

For a bad solvents inside the sphere, incoming error info F is:

$$f_i = e^{+(R_{ai} - R_o)} \qquad (8)$$

Such errors can be found sometimes for larger molecules such as plasticizers.

If the solvent point is placed on the sphere boundary, error distance becomes zero. This may occur for both good solvent and bad solvent [16].

In our program, we assumed the starting point based on average of HSP of all solvents. Hereafter, our method was different from Hansen's method to calculate HSP. Hansen performed his calculations by pseudo-optimization method and his results were not equal to 1.0 for F for many examples. In this work, we applied Nelder-Mead algorithm (available in MATLAB optimization toolbox) which has been presented by Lagarias et al [17] to minimize the Objective Function. For this optimization process, we defined the Objective Function as following form:

$$Objective\ Function = \left|F - 1\right| \quad (9)$$

Our aim was to find the global minimum of above mentioned function. After testing the program on some polymers, we found that the value of F in Eq (4) is a very important factor for calculating HSP. Hansen found the HSP in neighborhood of the answer region and didn't use the value of F as unity. This value has great influence on the calculated HSP and radius of solubility sphere.

Hansen examined 41 solvents on Polyethersulphone and calculated the HSP of it and R_a/R_o for each solvent. We recalculated HSP and R_a/R_o by our program with F = 1. Table (1) shows Hansen's and our results. Hansen's calculations was based on F = 0.999 and his results was 19.6, 10.8, 9.2, and 6.2 for δ_d, δ_p, δ_h, and R_o, respectively. These values by our program with F = 1 was 20.09, 10.63, 9.57, and 6.72, respectively. It's obvious that these values have noticeable differences in compare of Hansen's values.

As it is shown in Table (1), increasing the value of F by 0.001 increased the HSP and radius of solubility sphere of Polyethersulphone by 0.3-0.5.

To show the effect of changes in F value, we plotted the fluctuations of δ_d, δ_p, δ_h,, and R_o as a function of F in Fig (2), Fig (3), Fig (4), and Fig (5), respectively.

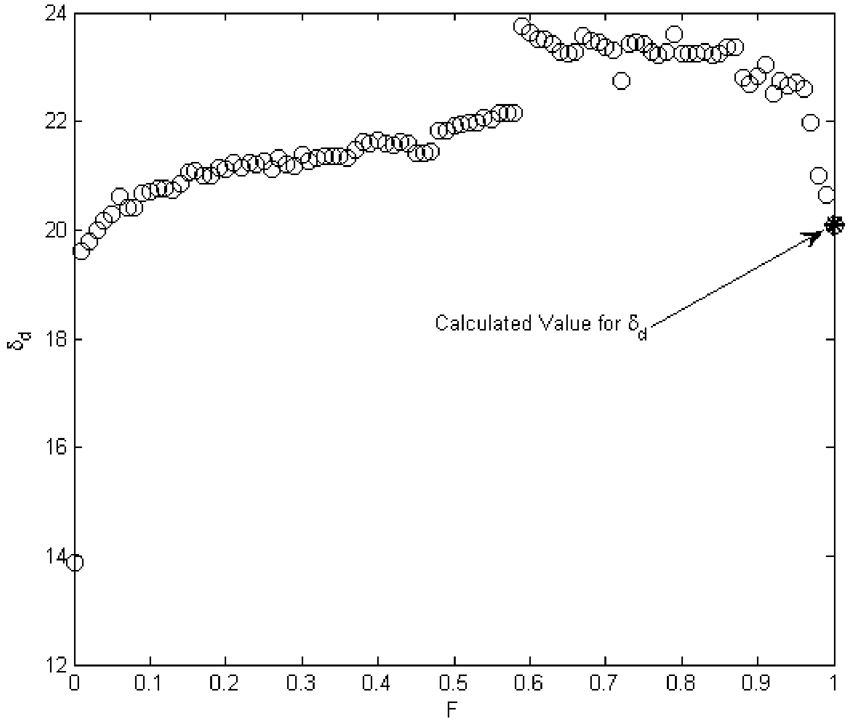

Figure 2 – Fluctuations of δ_d as a function of F.

Table-1 – Obtained values in this work in compare of Hansen's Results

[1]Hansen [15]:

F=0.999 δ_d=19.6 δ_p=10.8 δ_h=9.2 Ro=6.2

[2]This Work:

F=1 δ_d=20.09 δ_p=10.63 δ_h=9.57 Ro=6.72

Solvent	δ_d	δ_p	δ_h	**Solubility**	**Ra/Ro**[1]	**Ra/Ro**[2]
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
gamma-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
Ethanolamine	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

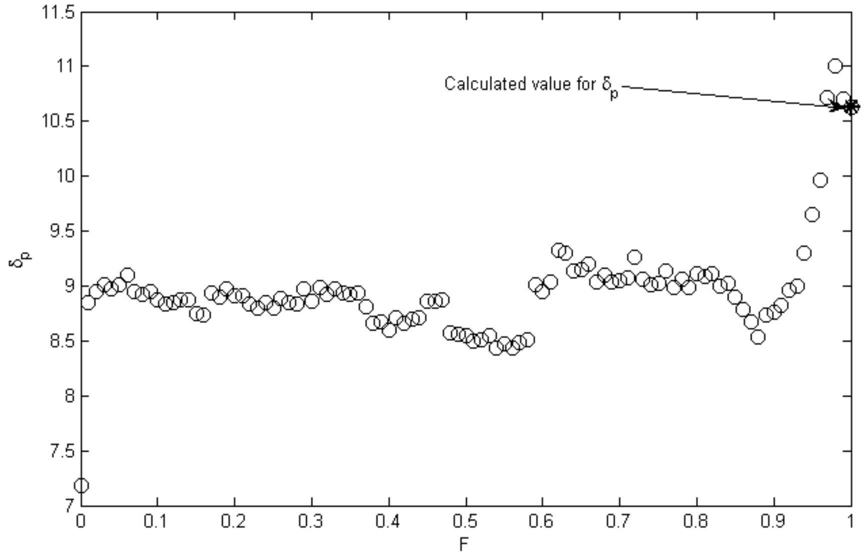

Figure-3 – Fluctuations of δ_p as a function of *F*.

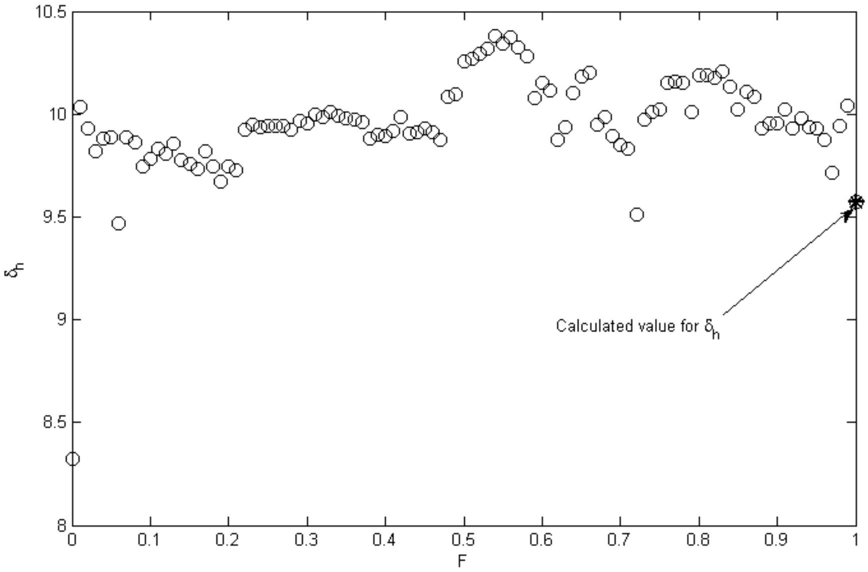

Figure-4 – Fluctuations of δ_h as a function of *F*.

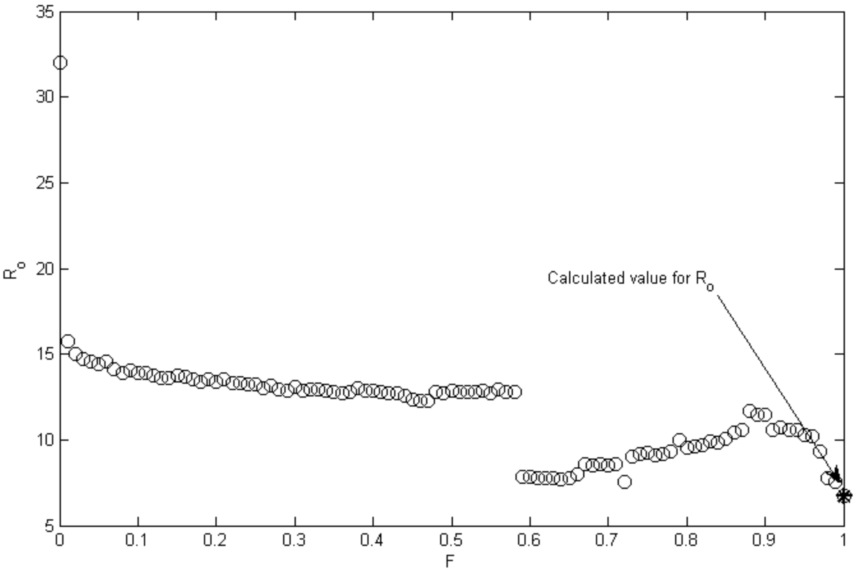

Figure-5 – Fluctuations of R_o as a function of F.

Conclusion

The method presented in this paper calculates more precisely the Hansen solubility parameters and radius of solubility sphere of a polymer or other solutes, based on original work of Hansen, with an improved mathematical method. As is explained and shown in Table (1) and Figs (2-5), the value of DataFit, *F*, is the most important parameter in calculation of HSP. Small deviation from unity in the value of *F*, causes noticeable changes in calculated HSP and radius of solubility sphere of solute.

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