Critical Analysis of the Graphical Determination of Hansen's Solubility Parameters for Lightly Crosslinked Polymers

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SYNOPSIS

The most widely accepted method for determining Hansen's three-dimensional solubility parameters (3DSP) for crosslinked polymers entails graphically estimating the center of a spherical region in 3DSP-coordinate space whose boundaries are defined in terms of the extent of swelling by solvents whose 3DSP values are known. In this article, the results of immersion tests performed at 25°C with 53 solvents on each of four commercial polymeric glove materials are used to critically evaluate this method. Analyses reveal a number of serious shortcomings with respect to the reliability of 3DSP estimates obtained. In the context of modeling solubility or other measures of solvent–polymer compatability, it is recommended that alternative methods be sought for determining 3DSPs for crosslinked polymers. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The three-dimensional solubility parameters (3DSP) developed by Hansen[1-4] for characterizing the interactions of solvents and polymers have received considerable attention over the past 30 years.[5] The concept of the 3DSP grew out of efforts in the late 1960s[6-9] to extend the regular solution theory of Hildebrand and Scott[10,11] to solvent–solvent and solvent–polymer systems where polar and hydrogen-bonding intermolecular interactions are important. According to the theory, both the enthalpy and free-energy changes that accompany the mixing of two materials are minimized when their respective solubility parameters are equal. Under this condition, the miscibility or solubility of the components is thermodynamically most favored. It follows that there should be an inverse relationship between the difference in the solubility parameters of two materials and their mutual solubility. This simple premise forms the basis for most of the published applications of Hansen's 3DSPs to mixtures of solvents and polymers.[5]

According to Hansen,[4] the total cohesive energy density of a substance, $\Delta E_V / V$, can be described as follows:

$$(\Delta E_V / V)^{1/2} = \delta_t = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2} \qquad (1)$$

where ΔE_V is the molar heat of vaporization (J/mol); V, the molar volume (cm^3/mol); δ_t, the total solubility parameter (MPa$^{1/2}$); and δ_d, δ_p, and δ_h (MPa$^{1/2}$), the partial 3DSPs which nominally represent dispersion, dipole–dipole, and hydrogen-bonding contributions, respectively. The difference in the 3DSPs of two materials, 1 and 2, can be calculated as

$$A = \delta_1 - \delta_2 = [a(\delta_{d1} - \delta_{d2})^2 + b(\delta_{p1} - \delta_{p2})^2 + b(\delta_{h1} - \delta_{h2})^2]^{1/2} \qquad (2)$$

where a and b are empirical weighting factors.[12]

Values of the 3DSPs for a large number of organic solvents and several uncured polymers were determined by Hansen on the basis of extensive

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solubility testing.[2,4] The δ_d values for the solvents were assigned according to their respective hydrocarbon homomorphs, after the method of Blanks and Prausnitz.[6] The δ_p and δ_h values were then determined from the polymer solubility tests by an iterative graphical approximation procedure. Through this empirical process, Hansen found that a more-or-less spherical region in 3DSP coordinate space emerged for a given polymer where the critical radius, A_c, defined the boundary between solvents in which the polymer was soluble and insoluble. The coordinates of the center of this solubility zone were designated as the polymer 3DSP values.

Beerbower and Dickey applied a similar graphical 3DSP analysis to systems of solvents and crosslinked polymers.[13] Results of immersion tests of polymer samples in a series of solvents were used to graphically delineate rectangular domains in 3DSP coordinate space which contained the solvents that swelled a given polymer by 25% or more. The value of the 25% swell was chosen as a discriminant value for their particular study which was concerned with selecting solvent-resistant materials to be used as equipment seals in systems containing lubricants. The "centroid" of this region, as defined using a subset of solvents which swelled the polymer greatly, was used to assign 3DSP values to the crosslinked polymer. Analogous approaches were used by other researchers to assign 3DSPs to polymeric chemical protective clothing materials and to characterize their resistance to swelling or permeation by organic solvents.[14-22] Those studies, however, typically used spherical zones and defined the polymer 3DSPs by various, often unspecified, criteria.

We recently explored a 3DSP-based approach to modeling the solubilities and permeation rates of organic solvents in crosslinked polymers using test samples cut from Viton® gloves.[12,23] The Viton 3DSP values used were those published by Perkins et al.[16] To apply these models to other common glove materials, it was necessary to determine the glove 3DSPs. Attempts to implement the graphical 3DSP estimation method described in the literature,[3-5,13-16] however, led to ambiguous results. It became apparent that the reliability of this method, and of the published 3DSP values based on this method, had never been verified. This article is the first of two which address this issue. In this article, we critically analyze this method of estimating 3DSPs for crosslinked polymers. In the following article, we explore a number of alternative methods that might be used for this purpose.

EXPERIMENTAL

Immersion tests were performed on four different polymers with the 53 solvents listed in Table I. All solvents were used as received from the Aldrich Chemical Co. (Milwaukee, WI) and were $\geq 96\%$ pure. The polymer materials consisted of commercial glove samples of butyl rubber (Model B-161, North Hand Protection, Charleston, SC), natural rubber (Model L-118, Pacific White, MAPA-Pioneer Industrial Products, Willard, OH), neoprene (Model 29-840, Ansell Edmont Industrial, Coshocton, OH), and nitrile (Model 37-155, Sol-Vex®, Ansell Edmont). All gloves were unsupported and unlined. Residual talc on the butyl gloves was removed with a damp cloth followed by drying at room temperature.

The glove samples were allowed to equilibrate at room temperature and ambient relative humidity for at least 24 h prior to testing. Rectangular samples measuring approximately 9×1 cm and weighing between 0.30 and 0.40 g were cut from the gauntlet regions of the gloves, preweighed on an analytical balance, and immersed in approximately 40 mL of solvent in a sealed Erlenmeyer flask. At least two tests were conducted for each solvent/glove combination using samples cut from different gloves. The flasks were placed in a thermostatted water bath at 25°C for 5 days. Samples were then removed from the flask, gently blotted to remove residual solvent from the surface, weighed, and placed in a vented oven at 70°C for 2 days. The samples were then reweighed and the difference between the final weight and the weight measured directly after immersion was used to determine the amount of solvent absorbed by the glove sample. Fractional weight changes as small as 0.03% could be measured, since the resolution of the balance was ±0.1 mg. Thus, accuracy and precision were limited by interglove production variations and the ability to reproducibly remove excess solvent from the sample surfaces.

The postdrying weight was used instead of the preexposure weight as the basis for determining the amount of solvent uptake because it accounts for any possible leaching of material from the glove samples during the immersion test. Comparisons made between preimmersion and postdrying weights indicated some loss in weight in most samples. In most cases, this was less than 3%, but in others, it was >10%. The drying process itself was found to have a negligible effect on the weights of the glove samples. None of the gloves contained plasticizers, so the weight loss was probably due to extraction of small quantities of compounding agents, dyes, or

other processing residues. In the case of the butyl and neoprene gloves, certain solvents turned amber over the course of the experiments apparently due to extraction of carbon black. With the exception of the tests involving nitrile with the aldehydes in which gross decomposition of the glove samples was apparent, all samples were recovered intact from the immersion tests.

To better assess the variability in the method and/or the glove samples, immersion tests were performed on five pairs of samples of the same glove material, where one member of each sample pair was cut from one glove and the second was cut from a different glove. Two sets of samples were tested in the case of natural rubber (i.e., with cyclohexane and ethanol) and nitrile (i.e., with benzene and ethanol) and three sets were tested in the cases of butyl rubber (i.e., with cyclohexane, dimethylformamide, and trichloroethylene) and neoprene (i.e., with benzene, ethanol, and nitropropane). The solvents chosen for these tests spanned a range of solubility values for each glove material.

RESULTS AND DISCUSSION

Immersion Tests

Table I lists the average percent weight gain calculated from replicate measurements ($n = 2$–14) for each solvent/glove combination. Weight gains ranged from 0.8% for ethanol in butyl rubber to 887% for chloroform in nitrile. Relative standard deviations (rsd) were $\leq 10\%$ for 203 of the 212 (96%) solvent/glove combinations. Most of the remaining combinations had rsd values $\leq 18\%$.

Tests of variability in solvent uptake between samples cut from two different gloves composed of the same polymer were performed using a paired t-test. Only one combination, trichloroethylene with butyl rubber, showed a significant difference in the averages from different gloves ($p = 0.03$). Considering that the overall average weight gain was 494% and that the difference between the two averages was less than 4%, this result is of little practical consequence. It seems reasonable to conclude that solvent uptake is not significantly affected by production variations within the lots of gloves used in this study and that the immersion testing can be performed with adequate reproducibility.

Defining the Zone

For our initial attempt to establish the spherical solubility zone which is required in the graphical

3DSP estimation method, we applied a minimum solvent uptake criterion of 10%. As suggested by previous reports,[3-5,13-16] the partial 3DSPs of the solvents (Table I) were displayed in three two-dimensional plots for each glove material: $2\delta_d$ vs. δ_p, $2\delta_d$ vs. δ_h, and δ_p vs. δ_h. All the solvent δ_d parameter values were doubled to render the plots involving this parameter more symmetrical. This is necessary because the range over which δ_d varies is much smaller than that of δ_p or δ_h.[3] Each point on the plots was labeled with the corresponding fractional weight gain from the solvent immersion tests (Table I), and the smallest circles containing the 3DSP values of all the solvents that met or exceeded the 10% weight gain criterion were constructed.

The stipulation of making the circles as small as possible has not been explicitly mentioned in any of the previous reports employing this method, and it is apparent in some reports[14-16] that other factors were considered in establishing the circle sizes and locations. The lack of a well-defined protocol for constructing these plots imparts a degree of inherent inaccuracy to the method and to the 3DSP values derived from it. Minimizing the size of the circle, as we have done here, results in an unambiguous determination of the center and radius.

Defining each circle was still a cumbersome process that required a certain amount of trial and error. The smallest circle that encompassed all the solvents meeting the specified uptake criterion was determined using one of two methods. In the first method, the two solvents whose coordinates were the most distant were used to define the diameter of the circle. The radius and center were then calculated. The Euclidean distance between the center of the circle and each of the solvents which met the uptake criterion was then calculated. If these distances were all less than the radius, then the circle was accepted as the smallest possible. This was the case in six of the 12 plots generated. If any of these distances were greater than the radius, then the second method of locating the circle was used.

With the second method, the following equation is used to select the three points that define the smallest circle which encompasses all the solvents meeting the uptake criterion:

$$x^2 + y^2 + \alpha x + \beta y + \gamma = 0 \qquad (3)$$

where x and y are the partial solvent 3DSPs corresponding to a point on the circle, and α, β, and γ are coefficients determined by solving the equation simultaneously for the three pairs of x and y values.[24]

Table I Solvent 3DSP Values and Immersion-test Fractional Weight Gains (%) in Each Glove Material at 25°C[a]

Solvent	3DSP Values (MPa$^{1/2}$)[b]			Percent Weight Gain							
	δ_d	δ_p	δ_h	Butyl		Natural		Neoprene		Nitrile	
n-Hexane	14.9	0.0	0.0	115	(3.6)	114	(3.8)	17	(1.3)	6.7	(4.7)
n-Heptane	15.3	0.0	0.0	141	(0.8)	134	(5.9)	17	(0.3)	6.1	(3.1)
Cyclohexane	16.8	0.0	0.2	265	(1.5)	251	(5.2)[d]	69	(0.5)	13	(1.2)
Methylcyclohexane	16.0	0.0	1.0	259	(1.7)	249	(3.0)	57	(1.1)	12	(0.4)
Benzene	18.4	0.0	2.0	114	(5.3)	283	(1.0)	217	(3.2)[d]	156	(3.0)[d]
Toluene	18.0	1.4	2.0	179	(4.7)	322	(0.6)	227	(6.6)	128	(0.1)
o-Xylene	17.8	1.0	3.1	226	(1.3)	327	(0.0)	272	(0.5)	126	(3.1)
Mesitylene	18.0	0.0	0.6	236	(2.6)	325	(4.6)	259	(0.2)	70	(2.1)
Triethylamine	17.8	0.4	1.0	171	(1.4)	198	(1.6)	69	(7.4)	22	(16.2)
n-Butylamine	16.2	4.5	8.0	81	(2.2)	177	(18.5)	240	(3.3)	174	(5.5)
Diethylamine	14.9	2.3	6.1	119	(3.8)	166	(0.7)	99	(9.3)	45	(5.5)
Dimethylformamide	17.4	13.7	11.3	2.8	(13.6)[d]	11	(7.4)	55	(2.2)	428	(0.3)
Formamide	17.2	26.2	19.0	1.9	(34.3)[c]	6.4	(9.6)	18	(0.6)	14	(8.0)
N-Methyl-2-pyrrolidone	18.0	12.3	7.2	6.7	(22.5)	22	(11.5)	206	(3.5)	798	(1.0)
2-Pyrrolidone	19.4	17.4	11.3	5.2	(9.8)	16	(9.2)	32	(0.7)	304	(4.3)
N,N-Dimethylacetamide	16.8	11.5	10.2	4.9	(6.0)	13	(4.5)	179	(0.9)	548	(1.6)
Acetone	15.5	10.4	7.0	5.1	(2.9)	15	(6.3)	29	(7.8)	163	(0.3)
Methyl ethyl ketone	16.0	9.0	5.1	11	(0.4)	42	(2.6)	85	(6.0)	247	(5.9)
3-Pentanone	15.8	7.6	4.7	22	(1.4)	115	(7.2)	156	(3.2)	251	(3.4)
Cyclohexanone	17.8	6.3	5.1	28	(1.7)	206	(4.5)	307	(3.6)	508	(0.7)
Methyl acetate	15.5	7.2	7.6	9.2	(0.2)	26	(1.5)	41	(9.1)	141	(4.1)
Ethyl acetate	15.8	5.3	7.2	15	(1.5)	60	(0.7)	65	(3.1)	133	(7.7)
Ethyl formate	15.5	8.4	8.4	9.7	(7.7)	29	(0.3)	37	(0.6)	288	(5.0)
Diethyl carbonate	16.6	3.1	6.1	15	(0.1)	64	(0.7)	82	(1.9)	106	(1.2)
Tetrahydrofuran	16.8	5.7	8.0	179	(6.7)	308	(3.8)	291	(0.6)	352	(0.4)
Dioxane	19.0	1.8	7.4	19	(0.2)	135	(2.1)	220	(6.0)	263	(1.8)
Ethyl ether	14.5	2.9	5.1	41	(5.8)	96	(3.4)	44	(0.9)	25	(0.5)
Nitrobenzene	20.0	8.6	4.1	11	(6.5)	99	(3.3)	247	(1.0)	546	(0.7)
Nitromethane	15.8	18.8	5.1	1.4	(2.5)	3.5	(5.1)	7.3	(9.3)	151	(0.2)
2-Nitropropane	16.2	12.1	4.1	5.8	(2.8)	26	(1.8)	55	(0.6)	345	(2.9)
Nitroethane	16.0	15.5	4.5	2.7	(5.2)	9.4	(3.5)	22	(8.2)	320	(7.9)
Butyraldehyde	14.7	5.3	7.0	17	(0.5)	88	(1.0)	155	(6.6)	297	(3.2)
Benzaldehyde	19.4	7.4	5.3	14	(1.0)	104	(4.2)	339	(9.9)	509	(1.6)
Furfural	18.6	14.9	5.1	4.5	(4.3)	9.2	(8.2)	37	(4.3)	458	(8.2)
2-Methoxyethanol	16.2	9.2	16.4	1.5	(10.4)	5.4	(4.8)	13	(0.8)	90	(4.7)
2-Butoxyethanol	16.0	5.1	12.3	6.2	(14.3)	26	(0.7)	42	(0.7)	47	(0.4)
2-Ethoxyethanol	16.2	9.2	14.3	2.3	(5.4)	9.8	(14.2)	23	(2.6)	64	(0.1)
2-(2-Methoxyethoxy)ethanol	16.2	7.8	12.6	1.8	(2.0)	6.4	(0.9)	23	(3.2)	119	(3.7)
Acetonitrile	15.3	18.0	6.1	1.3	(12.0)[c]	2.6	(6.2)	7.3	(4.7)	78	(2.5)
Propionitrile	15.3	14.3	5.5	1.9	(3.0)	6.0	(8.9)	17	(0.5)	162	(1.2)
Butyronitrile	15.3	12.4	5.1	3.5	(9.7)	15	(4.1)	34	(9.1)	226	(1.6)
Benzonitrile	17.4	9.0	3.3	9.5	(6.6)	105	(0.9)	196	(1.9)	521	(1.6)
Methylene chloride	18.2	6.3	6.1	104	(5.1)	343	(8.3)	241	(0.6)	614	(7.3)
Chloroform	17.8	3.1	5.7	339	(5.7)	528	(3.1)	435	(5.0)	887	(7.2)
Carbon tetrachloride	17.8	0.0	0.6	460	(1.2)	691	(5.0)	377	(1.4)	102	(1.8)
1,2-Dichloroethane	19.0	7.4	4.1	37	(1.3)	196	(2.9)	233	(1.3)	609	(2.6)
1,1,1-Trichloroethane	16.8	4.3	2.0	357	(3.4)	470	(3.5)	311	(2.4)	211	(1.3)
Perchloroethylene	19.0	6.5	2.9	578	(2.1)	719	(4.2)	405	(1.3)	72	(0.8)
Trichloroethylene	18.0	3.1	5.3	494	(2.1)[d]	618	(1.3)	387	(5.3)	333	(6.0)

(*Continued*)

Table I *(Continued)*

Solvent	3DSP Values $(MPa^{1/2})^b$			Percent Weight Gain			
	δ_d	δ_p	δ_h	Butyl	Natural	Neoprene	Nitrile
Methanol	15.1	12.3	22.3	1.1 (0.7)	3.0 (9.2)	13 (5.6)	20 (0.9)
1-Propanol	16.0	6.8	17.4	1.6 (0)	7.7 (5.2)	7.2 (5.1)	25 (1.0)
1-Butanol	16.0	5.7	15.8	2.1 (5.3)	11 (7.4)	8.2 (5.1)	27 (2.7)
Ethanol	15.8	8.8	19.4	0.9 (5.0)	3.6 $(6.5)^d$	6.1 $(7.8)^d$	23 $(2.4)^d$

[a] Values in parentheses are relative standard deviations in percent ($n = 2-4$ except where indicated).
[b] From Ref. 4.
[c] $n = 6$.
[d] $n = 10-14$.

The center of the circle corresponds to the value of $x = -\alpha$ and $y = -\beta$, and the radius, A_p, is given by

$$A_p = (\alpha^2 + \beta^2 - \gamma)^{1/2} \qquad (4)$$

where the subscript p reflects the weight-percent uptake criterion used to define the radius (see below).

A circle was constructed for each possible set of three points and was checked to determine if it encompassed all the required points. If more than one circle circumscribed all of the points, the circle with the smallest diameter was used. Regardless of whether two or three points were used, the center and A_p of each of the three circles corresponding to a specific glove material were calculated.

Figure 1(a)–(c) presents circular plots for the butyl rubber glove material generated by applying the 10% uptake criterion as just described. Estimates of each partial 3DSP were obtained from two of the three plots. In most cases (i.e., 8 of 12), the two estimates differed by less than 0.8 MPa$^{1/2}$ (note: this was also true when using other uptake criteria). The largest difference was 3.7 MPa$^{1/2}$, which occurred with the δ_p estimate for nitrile. In general, however, the δ_h values were the most disparate with differences typically in the range of 0.7–1.9 MPa$^{1/2}$. Regardless, the final set of 3DSP values for each polymer was obtained by averaging the pairs of individual values. These data are provided in Table II for each glove and several different uptake criteria.

Determining an A_p value for the sphere required additional calculations because the radii of the three circles differed, reflecting the fact that the zone was not perfectly spherical. In some cases, e.g., A_{10} for nitrile, the zone could not be considered even approximately spherical (see Table II), nor could it be resolved into two separate zones as suggested in another study.[13] Reconciling these differences by averaging the three circle radii was not acceptable because it resulted in a sphere that excluded solvents meeting the uptake criterion. Instead, A_p was assigned the radius of the smallest sphere centered on the average 3DSP values which still contained all solvents meeting the minimum solvent uptake criterion. As a result, the final A_p for the sphere was greater than all the circle radii.

A slightly more efficient approach to defining A_p entails creating the spherical solubility zone directly in three dimensions using logic similar to that just described for defining the locations of the circles in two dimensions. For example, a sphere can be constructed using the two most distant points in 3DSP space.[25] But this does not ensure that all points meeting the required uptake criterion will be enclosed in the sphere. At least four points on the perimeter of the sphere must be defined to ensure that all the solvents meeting the uptake criterion are included within the zone.

A more subtle factor affecting the determination of the 3DSP and A_p values is the way in which the uptake criterion is applied to define the zone. If, as was done here, A_p is determined such that all solvents meeting or exceeding a certain uptake level are included within the sphere, then it is invariably the case that solvents which fail to meet this criterion are also included within the zone. As shown in Table II, the number of incorrectly classified solvents ranged from 2 to 11, depending on the uptake criterion.

Although this is not unusual, it does raise the question of how to deal with misclassified solvents. In the report of Bentz and Billing,[14] a number of solvents belonging within the spherical zone were excluded apparently to avoid including other solvents which did not belong within the sphere. This practice is not recommended since it renders the
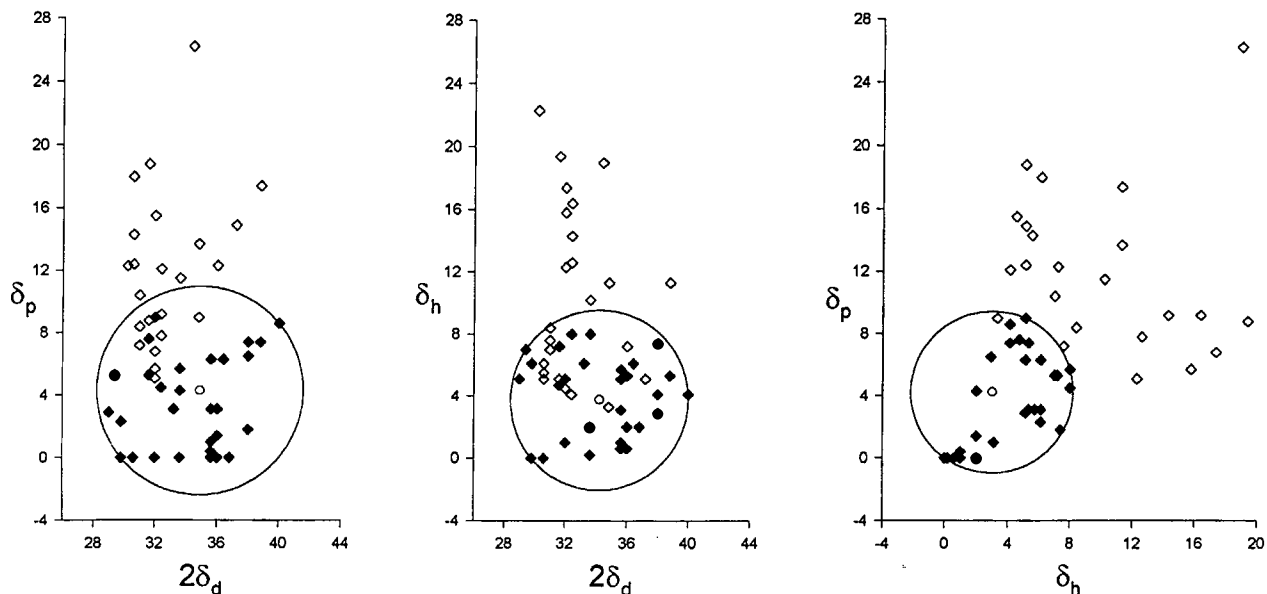
Figure 1 Two-dimensional plots of solvent 3DSP values ($MPa^{1/2}$) and the corresponding circular boundaries defined using a criterion of 10% (by weight) minimum solvent uptake in butyl rubber glove samples: (a) $2\delta_d$ vs. δ_p; (b) $2\delta_d$ vs. δ_h; (c) δ_p vs. δ_h. Filled symbols designate $\geq$ 10% uptake and open symbols designate < 10% uptake (O = center point).

3DSP determinations arbitrary. Adhering to the rule that the sphere *must* contain all solvents meeting the uptake criterion avoids this problem.

The complementary criterion of *excluding* all solvents that do not meet the specified uptake percentage was also considered. Establishing 3DSPs in this way was very difficult. As shown in Figure 1(a), while there is a clearly identifiable cluster of solvents meeting the 10% uptake criterion, drawing a circle that completely excludes the other solvents is not possible without also excluding a large fraction of the solvents that belong within the circle. Figure 1(b) illustrates a case where it would be virtually impossible to draw a circle meeting the complementary criterion, since the correctly and incorrectly classified solvents are freely interspersed. This approach is therefore not recommended.

Effect of Boundary Uptake Criterion on 3DSP Estimates

It is assumed with this method that the 3DSP estimates are independent of the uptake percentage chosen to define the boundary of the spherical zone. In other words, the spherical regions defined by different degrees of swelling are assumed to be concentric.[13] But this has never been demonstrated. Perkins et al.[16] reported averaging the values of the center points of 3DSP plots determined from three

different uptake percentages for solvents in Viton in an apparent attempt to account for differences in their locations. But the ranges of values obtained and the implications in terms of the reliability of the estimates were not discussed. Beerbower and Dickey alluded to using only the highest swelling solvents in determining the 3DSP values of the polymers in their study.[13] Bentz and Billing, on the other hand, based their determinations on the 10% uptake criterion only.[14] Other reports on graphical 3DSP determinations of crosslinked polymers did not discuss the uptake criteria employed.[3,15,19,20]

To examine the effect of changing the uptake criterion on the resulting 3DSP values for the four glove materials used in this study, the method described above for defining the spherical zone at 10% uptake was applied to uptake percentages of 25, 50, 100, and 200%. Table II summarizes the results in terms of the 3DSP values, A_p values, and the number of misclassified solvents for all these criteria. Figure 2(a)–(c) illustrates for butyl rubber the two-dimensional plots and the corresponding center points for three of these uptake levels. As shown, the estimates of the polymer 3DSPs can depend strongly on the chosen uptake criterion. The change in 3DSP values is particularly large on going from 10 to 25% uptake for all the glove materials. Changes in δ_p and δ_h are typically larger than those in δ_d, as expected. Although averaging the estimates determined at different up-

Table II   Graphical Estimates of Polymer 3DSP Values Based on Different Minimum Solvent-uptake Criteria[a]

Glove Material	Uptake Criterion (%)	n_i	n_0	3DSP Values (MPa$^{1/2}$)			Circle Radii (MPa$^{1/2}$)			Sphere Radius (MPa$^{1/2}$)
				δ_d	δ_p	δ_h	$2\delta_d$ vs. δ_p	$2\delta_d$ vs. δ_h	δ_p vs δ_h	
Butyl										
This study	10	29	2	17.3	4.3	3.4	6.7	5.8	5.2	7.2
	25	21	8	16.8	3.3	3.7	5.5	4.8	4.9	6.2
	50	18	7	16.8	3.1	3.7	5.2	4.8	4.9	6.1
	100	17	8	16.8	3.1	3.6	5.2	4.8	4.9	6.1
	200	9	5	17.5	3.1	2.4	4.4	3.2	3.6	4.6
Literature	10[b]			18.0	0.8	0.8				7.6
	25[c]			16.0	2.3	3.3				
	ns[d]			17.6	0.0	0.0				
	ns[e]			19.1	5.9	6.5				
Natural										
This study	10	41	9	16.7	8.6	6.8	9.8	8.2	10.4	11.6
	25	34	5	16.8	5.2	5.4	6.8	6.8	7.2	8.5
	50	29	2	17.3	4.1	3.5	6.7	5.8	5.1	7.2
	100	24	6	17.1	3.8	3.5	5.8	5.5	5.1	6.7
	200	14	5	17.4	3.1	4.1	4.4	4.0	4.8	5.2
Literature	25[c]			18.4	2.0	7.2				
	ns[f]			17.4	3.1	3.1				7.0
	ns[g]			19.2	2.0	2.0				
Neoprene										
This study	10	48	5	16.3	13.0	10.3	13.4	11.3	16.2	16.8
	25	39	8	17.5	8.7	6.1	9.3	6.4	10.3	10.8
	50	31	8	17.3	6.3	6.3	6.3	5.6	8.7	9.0
	100	22	11	17.6	5.9	5.5	6.2	5.5	7.5	7.7
	200	18	11	18.0	6.2	4.5	4.0	4.4	7.0	7.3
Literature	25[c]			19.4	3.1	3.7				
	ns[g]			19.2	5.3	4.5				
Nitrile										
This study	10	51	2	16.8	11.3	10.5	9.8	11.2	16.1	17.2
	25	45	3	17.1	8.9	8.0	9.8	8.6	10.6	11.7
	50	40	8	16.8	9.0	7.2	9.8	8.2	10.2	11.4
	100	35	9	17.3	9.1	6.3	9.8	6.1	10.2	10.8
	200	23	10	17.8	9.8	7.4	8.1	5.7	8.2	9.1
Literature	25[c]			18.0	4.1	4.1				
	ns[f]			19.0	9.2	4.1				10.0
	ns[g]			19.2	10.6	6.3				

[a] n_i = number of solvents inside sphere that meet the uptake criterion; n_0 = number of solvents inside sphere that do not meet the uptake criterion; ns = not specified.
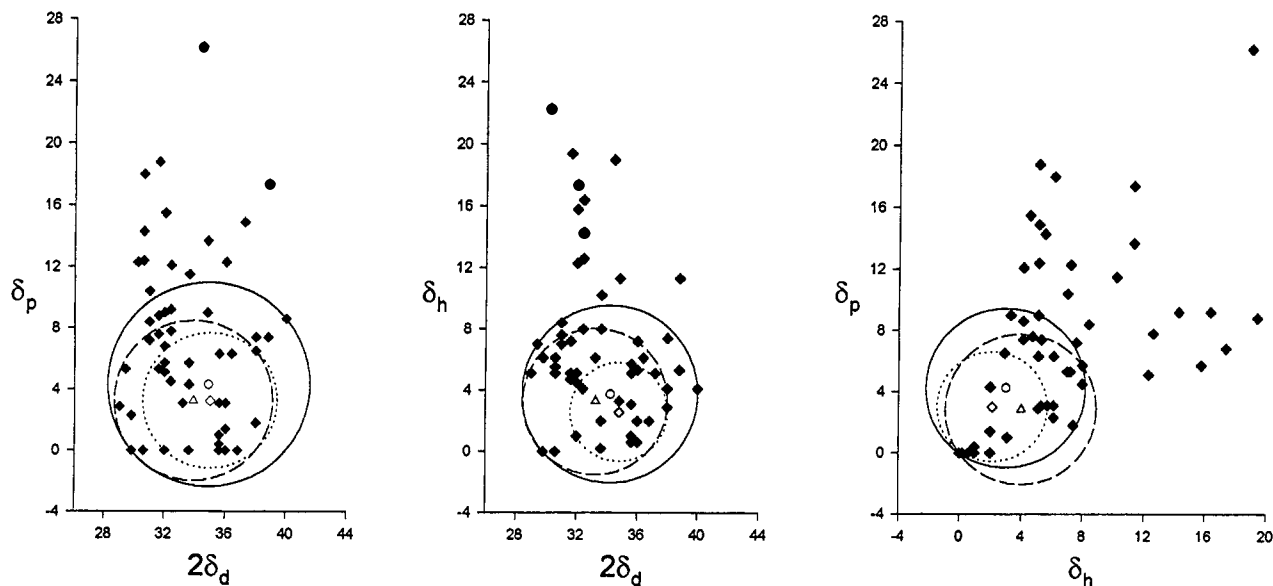[b] Ref. 14.
[c] Ref. 13.
[d] Ref. 9.
[e] Ref. 20.
[f] Ref. 4.
[g] Ref. 15.

Figure 2 Two-dimensional 3DSP plots for butyl rubber illustrating the effect of the selected uptake criterion on the location and radius of the circular discriminants: (· · · · ·, ◇) 200% uptake; (- - - -, △) 50% uptake; (——, ○) 10% uptake. Units are MPa$^{1/2}$.

take levels could be considered, it does not appear justified given the large ranges of values involved. In light of these results, it is difficult to place much confidence in the accuracy of 3DSP estimates determined by this or other similar graphical methods.

The effect of the uptake criterion on A_p is also noteworthy. Although the expected decrease in A_p with increasing uptake level is observed, the strength of the dependence varies greatly among the glove materials. For neoprene, A_p increases by more than a factor of two on going from 200 to 10% uptake, while for butyl, there is very little change in A_p over most of the uptake range. These findings tend to refute the commonly held notion that A can be used to discriminate between "relatively strong" and "relatively weak" solvent–polymer interactions. This concept is embodied in the so-called relative energy density (RED) suggested by Hansen as a semiquantitative index of interaction strength.[26,27] The RED is defined as A/A_c, where A_c is associated with some critical degree of interaction. If $A < A_c$ for two materials (i.e., if RED < 1), then their interaction is expected to be greater than if $A > A_c$. The data shown in Table II (and Fig. 3, see below) suggest that there is little basis for using the RED in such a manner.

### Correlation of Solvent Uptake with Proximity to the Center of the Zone

As stated above, most analyses employing 3DSPs rely on there being an inverse relationship between

A [from eq. (2)] for a given polymer–solvent pair and their mutual solubility or interaction strength. With the graphical 3DSP estimation method being considered here, it is implied that there is a *linear* relationship between A and solubility. Notwithstanding the lack of any theoretical justification for this assumption, the data collected here illustrate quite clearly that this is not the case. The presence of misclassified solvents within all of the spherical zones is the first evidence of this. Moreover, even those solvents correctly included within the zone do not follow the expected trend.

This point is illustrated in Figure 3 where A is plotted vs. solvent uptake for butyl rubber. Linear regression yielded a correlation coefficient (r^2) of only .237, indicating a very weak relationship between these variables. The slope is also very shallow. If consideration is restricted to the data above the 10% uptake level, the correlation is even poorer ($r^2 = .172$) and the slope is nearly zero. Regression analyses for the natural, neoprene, and nitrile gloves yielded similar results, with r^2 values of 0.378, 0.061, and 0.167, respectively. These data confirm similar findings that we reported for Viton.[23]

A further illustration of this point is found in Table III which presents the uptake percentages of those solvents used to define the locations and sizes of the 12 circles employed to determine the 3DSPs for uptake criteria of 10, 50, and 200%. With butyl rubber, e.g., the defining solvents for the 10% uptake criterion covered an uptake range of 10–179%. In
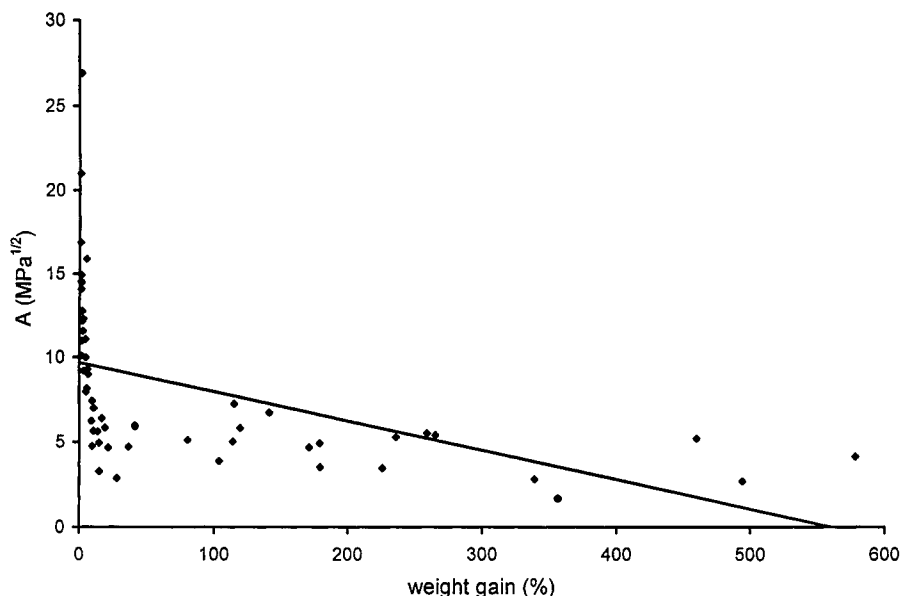
Figure 3 Plot of 3DSP difference [A from eq. (2)] vs. immersion-test weight gain for solvents in butyl rubber. Solid line was obtained from simple linear regression ($r^2 = .237$).

all but two cases, at least one of the defining solvents had an uptake of over 100%.

Although the approximate nature of graphically determining the boundaries of polymer solubility zones was acknowledged in the early reports by Hansen[3] and others,[13] it was implied in those studies that the exceptional cases were confined to the periphery of the established zones and that a progression should be observed toward lower solubility as A increased. However, in our plots, the exceptional solvents were not always found near the boundaries, and the correlation of swelling and A was not observed. These results raise further doubt about the reliability of this 3DSP estimation method and the use of the 3DSP difference alone as an index of solvent uptake in crosslinked polymers.

Effect of Excluding Certain Solvents on 3DSP Estimates

The number of solvents tested and the manner in which the data are utilized will also affect the final 3DSP values. While a fairly large number of solvents is needed to adequately span the range of possible 3DSP values (Hansen recommends 42 solvents[26]), the only solvents that really matter are the few that define the boundaries of the zone. Thus, the 3DSP determination will usually hinge on the presence or absence of certain critical solvents.

Formamide is an example of a critical solvent for neoprene as shown in Figure 4. This solvent has an

unusually large δ_p value, and despite the fact that its uptake in neoprene is 18%, it is one of the defining solvents for the 3DSP values when using a nominal minimum uptake criterion of 10%. The estimates of δ_p and δ_h change by 6.9 and 1.7 $MPa^{1/2}$, respectively, and A_{10} changes from 16.2 to 12.7 depending on whether formamide is used or not (see Fig. 4). Thus, this one solvent has a remarkably large effect on the value of the 3DSPs determined for neoprene. In other cases, exclusion of solvents may have little or no effect. From the data shown in Table III, hexane emerges as an important solvent in defining 3DSPs for three of the four gloves. If heptane had been used instead of hexane, the effect on the glove 3DSPs would be negligible because it has 3DSP values very similar to those of hexane and it gives similar weight changes in the glove samples. Formamide and hexane represent the two extremes in the effects of individual solvents on the determination of the polymer 3DSPs. This sensitivity to individual solvents in the data set reduces the reliability of the method.

Related to the preceding point is the inefficiency with which most of the data are utilized. Despite the fact that solvents included within the zone may differ in their uptake values by factors of 50 or more, they may have the same influence, or lack thereof, on the estimates of the polymer 3DSP values. Intuitively, one would expect that the 3DSPs for a polymer should be influenced more by those solvents providing a greater degree of swell. With this graphical method, there is no mechanism for weighting

Table III Solvents and Corresponding Fractional Weight Gains (%, in Parentheses) Used to Define the Circular Discriminants for Each of Three Nominal Minimum Uptake Criteria

Uptake Criterion (%)	Plot	Butyl	Natural	Neoprene	Nitrile
10	$2\delta_d$ vs. δ_p	n-Hexane (115) Nitrobenzene (11)	n-Hexane (114) 2-Pyrolidone (16)	Formamide (18) n-Hexane (17) Benzene (217)	Nitromethane (151) Benzene (156)
	$2\delta_d$ vs. δ_h	n-Hexane (115) Butyraldehyde (17) Nitrobenzene (11)	n-Hexane (114) Nitrobenzene (99) 1-Butanol (12)	Methanol (13) n-Hexane (17) Mesitylene (259)	Methanol (20) Mesitylene (70)
	δ_h vs. δ_p	n-Hexane (115)[a] Methyl ethyl ketone (11) Tetrahydrofuran (179)	n-Hexane (114)[a] 2-Pyrolidone (16) 1-Butanol (12)	n-Hexane (17)[a] Formamide (18)	Cyclohexane (13) Formamide (14)
50	$2\delta_d$ vs. δ_p	Perchloroethylene (578) n-Hexane (115)	n-Hexane (114) Nitrobenzene (99)	Dimethylformamide (55) Methylcyclohexane (56) Benzene (217)	Nitromethane (151) Benzene (156)
	$2\delta_d$ vs. δ_h	n-Hexane (115) n-Butylamine (81) Perchloroethylene (578)	Butyraldehyde (88) Nitrobenzene (99) n-Hexane (114)	Dimethylformamide (55) Cyclohexane (69) Nitrobenzene (247)	Butyraldehyde (297) Nitrobenzene (546) Mesitylene (70)
	δ_h vs. δ_p	n-Hexane (115)[a] Tetrahydrofuran (179)	n-Hexane (114)[a] Tetrahydrofuran (308) Benzonitrile (105)	Dimethylformamide (55)[b] Mesitylene (259)[b]	Nitromethane (151) 2-Methoxyethanol (90) Mesitylene (70)[b]
200	$2\delta_d$ vs. δ_p	Perchloroethylene (578) Methylcyclohexane (259)	Methylcyclohexane (249) Perchloroethylene (719)	Carbon tetrachloride (377) Benzene (217) N-Methylpyrrolidone (206)	Butyraldehyde (297) 2-Pyrrolidone (304) Dioxane (263)
	$2\delta_d$ vs. δ_h	Methylcyclohexane (259) Perchloroethylene (578) Chloroform (339)	Methylcyclohexane (249) Cyclohexane (251) Tetrahydrofuran (308)	n-Butylamine (240) Nitrobenzene (247) Mesitylene (259)	Butyraldehyde (297) Nitrobenzene (546) 2-Pyrrolidone (304)
	δ_h vs. δ_p	Chloroform (339) Perchloroethylene (578) Cyclohexane (265)	Cyclohexane (251) Tetrahydrofuran (308)	N-Methylpyrrolidone (206) Mesitylene (259)[b]	1,1,1-Trichloroethane (211) Dioxane (263) 2-Pyrrolidone (304)

[a] Heptane also met the uptake criterion and had the same δ_p and δ_h values.
[b] Carbon tetrachloride also met the uptake criterion and had the same δ_p and δ_h values.
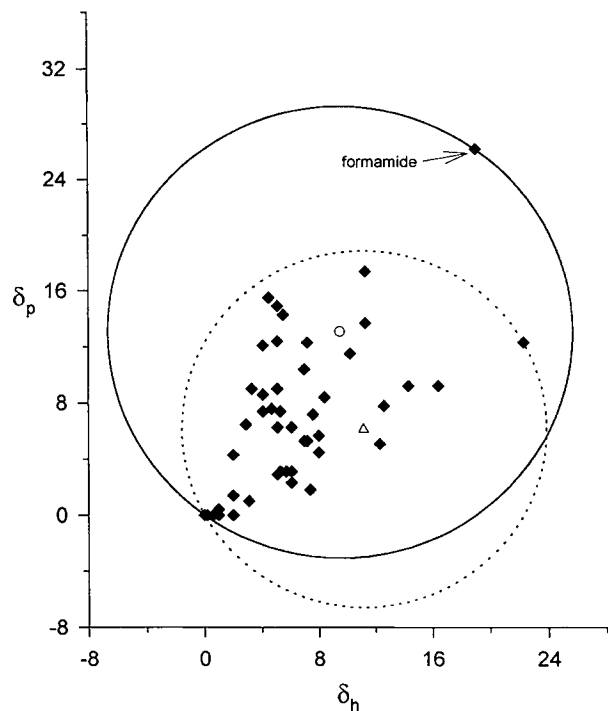
Figure 4 Effect of (———, O) including and (- - - -, △) excluding formamide in the data set on the location and size of the circular discriminant of δ_p vs. δ_h for neoprene using a 10% (minimum) uptake criterion.

the influence of the solvents according to their uptake.

Comparison with Published Polymer 3DSP Values

Included in Table II are 3DSP values determined by other researchers for the same or similar polymers using analogous graphical methods. As mentioned above, those from Bentz and Billing[14] were based on a 10% solvent uptake criterion, while those from Perkins et al.[16] were based on an average of several uptake criteria. References 15 and 19 did not specify the uptake criteria. All these studies employed spherical zones, although only Bentz and Billing reported values of A_p. Beerbower and Dickey,[13] again, used rectangular zones with a boundary criterion of 25% solvent uptake. Henriksen[20] reported values for several materials but did not describe the procedure employed for their determination. According to a later report,[15] the values used in Henriksen's study were determined by Hansen several years earlier on uncured samples of the same types of polymers.

As shown in Table II, the range of reported 3DSP values for a given type of polymer is quite broad. Although nominally the same type of polymer, the materials tested differed in certain cases. In other

cases, however, the same product was used. For example, the butyl rubber gloves used in this study are the same model as those used in the studies of Perkins et al.[19] and Bentz and Billing.[14] The nitrile and neoprene values from Perkins and Tippit[15] were obtained from the same models of gloves as used in this study. Although it might be argued that lot-to-lot differences among these products could account for the differences in 3DSP values, it is more likely that the differences are a result of the inherent inaccuracy of the graphical estimation method.

The large differences between the butyl rubber 3DSP and A_{10} values determined here and those reported by Bentz and Billing were particularly puzzling since the same glove model and a similar set of solvents were used. In attempting to superimpose their values of 3DSP and A_{10} for butyl rubber onto our data, we found that the number of misclassified solvents increased. In particular, 12 solvents that belonged within the sphere were now excluded. The lack of agreement in the butyl 3DSP and A_{10} values is thus apparently due to differences in the protocols used to define the spheres. Although it was evident from the figures presented in their article that they also allowed certain solvents which met the uptake criterion to remain outside their spherical zone, it was not possible to determine which, or how many, of their solvents were excluded.

CONCLUSIONS

The analyses presented in this article illustrate how the graphical estimation of 3DSP values for lightly crosslinked polymers is inherently inefficient and unreliable. Published 3DSPs determined with this method, including those reported for various chemical protective clothing materials, therefore should be viewed with skepticism. The lack of a well-defined protocol for 3DSP determinations of crosslinked polymers has undoubtedly contributed to the relatively poor performance of most 3DSP-based approaches to characterizing polymer–solvent solubility and permeation behavior.[16,18,22]

From a practical standpoint, the manipulations required to implement the graphical method are very cumbersome. A large number of immersion tests must be performed to ensure coverage of as much of the 3DSP coordinate space as possible. At the same time, only a small fraction of the data collected is actually used in the 3DSP determinations. Beyond establishing some arbitrary critical radius, the method ignores the relative solubilities of the different solvents: A solvent causing 200% swell is

given no more weight in determining the location of the polymer 3DSP value than one causing 20% swell.

Finally, the graphical method has only a very approximate basis in theory. It fails to account for the known influence of molar volume and crosslink density on solubility, and it incorrectly assumes an implicit linear relationship between the solubility parameter difference and solubility.

Alternative methods for estimating the 3DSPs are needed which are more efficient and are more consistent with known theories of polymer–solvent interaction phenomena. The next article discusses some possibilities.

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