Improved Methods for the Determination of Hansen's Solubility Parameters and the Estimation of Solvent Uptake for Lightly Crosslinked Polymers

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SYNOPSIS

Two new methods for determining Hansen's three-dimensional solubility parameters (3DSP) for lightly crosslinked polymers are presented and evaluated using commercial glove materials composed of butyl, natural, nitrile, and neoprene rubber. In the first method, the polymer 3DSPs are determined from a weighted average of the 3DSPs of a range of organic solvents, where the weighting factor is the product of the solvent molar volume and the fractional uptake of the solvent measured by immersion testing. The resultant polymer 3DSPs were used to model solvent uptake via the Hildebrand–Scott and modified Flory–Rehner expressions for the Flory interaction parameter. After grouping solvents of similar structure and applying an additional weighting factor, estimates of equilibrium solubility within a factor of two of experimental values were obtained for 176 of the 212 (83%) solvent–polymer combinations examined. In the second method of estimating polymer 3DSPs, the Flory interaction parameters for all solvent–polymer pairs are determined at the outset via the modified Flory–Rehner equation and used to solve for the polymer 3DSP values by multiple nonlinear regression. Solubility estimates are then back-calculated. This method provided different values of the 3DSPs for the polymers, including negative δ_p values for the butyl and natural rubber. However, the accuracy of solubility estimation was comparable to that obtained using the weighted-average method without the need for any adjustable factors. The advantages of these alternative methods over the graphical method for obtaining reliable estimates of the 3DSPs of lightly crosslinked polymers are discussed. This is the first demonstration of a general 3DSP-based approach to quantitative solubility modeling in polymer–solvent systems. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Numerous studies have shown that the interactions between organic solvents and polymers can be described with the aid of Hansen's three-dimensional solubility parameters (3DSP).[1–5] Yet, the 3DSP concept has been of limited value in applications where quantitative estimates of solubility are required. One factor contributing to this situation, particularly for cases involving crosslinked polymers, is the lack of a reliable means of determining the 3DSP values of the polymer.

The preceding article identified several problems with the graphical method of determining 3DSPs for crosslinked polymers.[6] Alternative methods for determining 3DSPs of polymers and oligomers have been reported on the basis of correlations with viscosity measurements of polymer solutions,[7] molecular group-contribution calculations,[8,9] and molecular simulation models.[10,11] However, none of these methods has been applied to crosslinked polymers or to problems involving quantitative estimates of solvent–polymer solubilities.

This study represents part of an on-going effort to develop generally applicable 3DSP-based models for predicting the solubility, and ultimately the permeation rate, of solvents in chemical protective

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elastomers.[12-14] Such models could be used to guide the selection of appropriate glove or suit materials for use in specific hazardous environments or in other critical applications involving contact of solvents with a crosslinked polymer.

Two alternative methods are explored here for determining the 3DSPs of lightly crosslinked polymers based on swelling data in a range of organic solvents. Commercial glove materials of butyl, natural, neoprene, and nitrile rubbers are used as the test samples. The 3DSP values obtained are then used to estimate the equilibrium solubility of the solvents in the polymers via well-known equations derived from the theories of Hildebrand et al.[15] and Flory and Rehner.[16,17]

THEORETICAL BACKGROUND AND METHOD DESCRIPTIONS

The concept of the 3DSP is based on the notion that the cohesive intermolecular forces of a substance can be expressed as the sum of three components.[1] If the total cohesive energy density of a volatile solvent is expressed in terms of the molar vaporization energy per unit volume, $\Delta E_V/V$, then the 3DSPs can be defined as[2]

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

where the subscripts d, p, and h designate the partial solubility parameters nominally corresponding to dispersion, dipole–dipole, and hydrogen-bonding forces, respectively. While most published solvent 3DSPs were actually assigned by Hansen et al. on the basis of empirical estimation procedures,[2,18,19] eq. (1) is still useful conceptually. Values of 3DSPs for polymers have been determined by various indirect methods, such as those discussed above and in the preceding article.[6]

As with many of the published methods of polymer 3DSP determination, the methods presented in this article rely on there being a relationship between the solvent and polymer 3DSPs and their mutual solubility. If the solvent is designated as component 1 and the polymer as component 2, then their 3DSP difference, A, can be determined using the following equation:

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

where the weighting factors a and b account for the influence of induced dipoles, orientational effects,

and other phenomena whose importance varies with the particular polymer–solvent combinations being considered.[1,18] Values of these weighting factors have been published for a number of different systems.[5,12,14,18,20-23] Typically, a is set equal to unity and b is in the range of 0.1–0.3, although values outside of this range have been reported.[12,22] The assignment of weighting factors remains empirical and is discussed below in the context of the 3DSP determination methods used here. The common practice of setting $a = 4$ and $b = 1$, which has been rationalized as a convenient way of making plots of 3DSPs more symmetrical,[1] is not recommended in the context of using 3DSPs to estimate solubility.[12]

In nearly all reports on 3DSPs, A has been used alone as a semiquantitative index of relative solubility: Higher A values imply lower mutual solubility and vice versa. However, the relationship between A and solubility is not as simple as assumed in such models. One means for relating A to solubility was explored in detail in our recent studies of solvent permeation through butyl and Viton® gloves.[12-14] It involves first relating A to the Flory interaction parameter, χ, by means of the following equation described by Hildebrand and Scott[15]:

$$\chi = \chi_s + V_1 A^2/(RT) \qquad (3)$$

where χ_s is a positive correction term which has been associated with entropic effects that arise in systems where dipolar and hydrogen-bonding interactions are significant. Lipson and Guillet suggested that other factors are also incorporated into this correction term.[24] It should be noted that eq. (3) was originally developed in the context of Hildebrand's regular solution theory using the Hildebrand solubility parameters.[15,25] Employing Hansen parameters in this expression was suggested many years ago,[1,26,27] but used for estimating 3DSPs and solvent–polymer solubility values only recently.[12,14] In these studies, it was assumed that $\chi_s = 0$.

The Flory interaction parameter for a given solvent–polymer pair can be related to their mutual solubility by the Flory–Rehner equation:

$$\chi = -2\nu V_1(\phi_2^{-5/3} - 0.5\phi_2^{-1})$$
$$- (\ln \phi_1)\phi_2^{-2} - \phi_2^{-1} \qquad (4)$$

where ν is the average polymer crosslink density (mol/cm^3) and ϕ_1 and ϕ_2 are the equilibrium volume fractions of the solvent and polymer, respectively.[16,25] Assumptions made in deriving eq. (4) are that there are four polymer segments emanating

from each point of crosslinking, the volume fraction of polymer is unity during the crosslinking process, and there is no change in the polymer free volume upon mixing with the solvent.[16]

More recent work has led to the modified Flory–Rehner equation

$$\chi = \frac{-(\nu F_\phi V_1 \phi_{2s}^{2/3} \phi_2^{1/3} + \ln(\phi_1) + \phi_2)}{\phi_2^2} \quad (5)$$

where ϕ_{2s} is the volume fraction of the polymer during the crosslinking process and F_ϕ characterizes the extent to which deformation in swelling approaches the so-called affine limit.[17,28] The latter variable can be estimated using the approach described in Ref. 28. This expression, although still approximate, provides a more accurate model than does eq. (4) for solvent–polymer interactions.

Use of eq. (5) to relate χ to ϕ_1 requires an independent estimate of the effective crosslink density of the polymer, which can be derived from stress–strain measurements at low degrees of elongation[29] or from immersion tests in a series of solvents whose χ values are known.[25] In a separate investigation, ν for the butyl, natural, neoprene, and nitrile glove materials used in this study were determined to be 1.6×10^{-4}, 2.2×10^{-4}, 2.5×10^{-4}, and 2.2×10^{-4} mol/cm^3, respectively.[30]

With this information, eq. (5) can be used to determine χ from experimental values of ϕ_1. This χ value can then be used in eqs. (2) and (3) to estimate polymer 3DSPs, provided that suitable values of the weighting factors can be found (see below). If the polymer and solvent 3DSPs are already known, then χ values can be calculated from eq. (3) and modeled values of ϕ_1 can be obtained from eq. (5).

3DSP Estimation Methods for Crosslinked Polymers

Among the recognized shortcomings of the graphical method for estimating the 3DSPs of crosslinked polymers are the lack of a theoretical basis for the assumed linear relationship between A and solubility, the failure to account for the influence of the solvent molar volume on the correlation between A and solubility, the critical dependence of the graphical determinations upon both the uptake criterion chosen to define the spherical solubility zone and the 3DSP values of only two or three "defining" solvents, and the cumbersome nature of the procedures involved. Alternative methods were sought that would utilize the immersion test data more efficiently and provide more stable 3DSP estimates.

The resulting 3DSPs also would be expected to find broader application in modeling the uptake of solvents by crosslinked polymers in the context of the equations presented above.

The first method considered here employs one of several weighted averages to estimate the polymer 3DSP values. These can be expressed in general form by the following equation:

$$\delta_{d2,p2,h2} = \frac{\sum\limits_{i=1}^{n} u_i V_{li}^z \delta_{(d1,p1,h1)_i}}{\sum\limits_{i=1}^{n} u_i V_{li}^z} \quad (6)$$

where, for a given polymer, u_i is the fractional uptake of solvent i expressed in terms of weight or volume and n is the total number of solvents tested. The exponential term z allows for adjustment of the weighting of the solvent molar volume. The subscripts on the δ terms in eq. (6) are used as shorthand notation to indicate that each of the partial 3DSP values of the polymer is determined separately from the weighted average of the corresponding partial 3DSPs of the solvents in the immersion-test data set.

The dependence of solvent uptake on the solvent molar volume was recognized by Hansen in his early studies, but it was never incorporated into his 3DSP estimation methodology.[3,4] In a more recent article, where permeation breakthrough times were used to define "effective" 3DSPs of protective clothing polymers, Hansen et al. suggested grouping solvents on the basis of molar volume to help address some anomalies in the data.[31,32] The reported approaches, however, do not provide a rigorous means of accounting for the solvent molar volume in relating 3DSPs to solubility or in determining polymer 3DSPs.

The second method for estimating 3DSPs explored in this investigation makes use of eqs. (3) and (5). Values of ϕ_1 are calculated for each solvent from the measured immersion-test weight gains. These are then used in eq. (5) to determine χ for each solvent–polymer pair. This χ value is then substituted in eq. (3) along with the solvent 3DSP values, leaving four unknowns consisting of the b weighting factor and the three polymer 3DSP values. It is assumed that $a = 1$, $\chi_s = 0$, and for a given polymer the same b weighting factor can be applied to all solvent–polymer pairs. A nonlinear regression analysis is then performed to solve for these unknowns using the data for all of the solvents in the data set simultaneously.

This regression method yields the set of polymer 3DSP values providing the minimum overall error between the X values used as input variables in the analysis [i.e., those calculated from the immersion test data via eq. (5)] and the corresponding modeled X values, which we designate as X_m. The residual errors that remain can be assigned to X_s. Alternatively, X_s can be determined explicitly by including it as a fifth unknown in the regression analysis. However, for the problems considered here, including X_s as a variable in the regression did not improve the precision of the estimates of the polymer 3DSP or b values. As a result, this option was not pursued further.

Modeling Solubility

Together with X values determined from experimental ϕ_1 values via eq. (5), the 3DSPs determined by the weighted-average method can be used in eqs. (2) and (3) to solve for b. In this case, each solvent–polymer pair will have a different b weighting factor. However, previous studies have shown that similar b factors are found within groups of solvents from the same chemical class.[12,22] If this were found to hold in general, it would allow the use of the same b weighting factor for several different solvents and it would permit the model to be used for the prediction of solvent–polymer solubilities of untested solvents.

The second method of estimating 3DSPs described above also comprises a model for estimating solubility. Once the 3DSPs and the b weighting factor for the polymer are determined, a value of X can be back-calculated from eq. (3) for any solvent. Equation (5) can then be used to determine a modeled ϕ_1, which can be converted to units of g/mL for comparison with experimental solubility data.

EXPERIMENTAL

Details of the immersion tests performed for this study are provided in the preceding article.[6] The polymer samples consisted of unlined, unsupported gloves composed of lightly crosslinked butyl (Model B-161, North Hand Protection, Charleston, SC), natural (Model L-118, Pacific White, MAPA-Pioneer Industrial Products, Willard, OH), neoprene (Model 29-840, Ansell Edmont Industrial, Coshocton, OH), or nitrile (Model 37-155, Sol-Vex®, Ansell Edmont) polymers. According to the manufacturer, the butyl rubber glove contains approximately 26% w/w of a carbon black filler. The remaining gloves

are unfilled. Table I presents the experimental solubilities, S_e, for all 53 solvents in terms of the mass of solvent per unit volume of polymer. The values presented are the averages of replicate fractional weight gain measurements ($n = 2$–14) multiplied by the corresponding polymer densities. For each polymer, the S_e values for the solvents span a range of 2–3 orders of magnitude.

The density of each glove material was estimated by water displacement at 25°C. For each glove type, 10 samples weighing approximately 3 g each were immersed individually in distilled water at 25°C and the volume displacement was measured to the nearest 0.2 mL. Average density values of 1.10, 1.00, 1.30, and 1.06 g/mL were obtained for the butyl, natural, neoprene, and nitrile rubber gloves, respectively. Relative standard deviations were less than 3% in all cases.

Statistical analyses were performed using Statgraphics® Plus (Version 6.0, Manugistics, Inc., Rockville, MD) and Microsoft Excel® (Version 5.0, Microsoft Corporation, Redmond, WA). For the nonlinear regression method used to estimate the polymer 3DSPs, an iterative search algorithm estimated the four variables (b and the three partial 3DSPs) by minimizing the residual sum of squares error between X and X_m. The graphically determined 3DSPs (10% uptake criterion)[6] and $b = 0.2$ were used as the starting values in the initial search procedure for each polymer. Since the estimate can depend on these starting values, several regressions were run with each data set using a range of starting values to ensure that the estimates were at the global error minimum, rather than at a local minimum. In all cases, the estimates of the polymer 3DSPs converged to within 1% of the final values reported below.

Values of ϕ_{2s} of 0.917, 0.935, 0.912, and 0.918 were calculated for butyl, natural, neoprene, and nitrile, respectively, from published polymer thermal expansion data[33–35] and processing information obtained from the manufacturers. Values of F_ϕ, estimated using the methods described in Ref. 28 and assuming that $\kappa = 20$ and $p = 2$, were 0.68 for butyl, neoprene, and nitrile and 0.69 for natural rubber.

RESULTS AND DISCUSSION

Polymer 3DSP Values Determined by the Weighted-average Method

3DSPs were calculated for each polymer by eq. (6) using four different weighting factors: fractional solvent uptake weight (w_1/w_2, $z = 0$); fractional

Table I Physical Properties and Solubilities at 25°C of the Solvents Used in this Study[a]

Solvent	Density (g/mL)	Molar Volume (mL/mol)	Experimental Solubility (S_e, g/mL)			
			Butyl	Natural	Neoprene	Nitrile
n-Hexane	0.659	131.31	1.26	1.13	0.220	0.072
n-Heptane	0.684	147.01	1.55	1.33	0.230	0.065
Cyclohexane	0.778	108.86	2.90	2.50	0.900	0.140
Methylcyclohexane	0.770	128.18	2.84	2.48	0.740	0.130
Benzene	0.879	89.48	1.25	2.82	2.84	1.66
Toluene	0.867	106.56	1.97	3.21	2.96	1.36
Xylene	0.897	121.14	2.47	3.25	3.56	1.34
Mesitylene	0.864	139.52	2.58	3.23	3.38	0.740
Triethylamine	0.726	139.67	1.87	1.98	0.900	0.230
n-Butylamine	0.740	98.76	0.880	1.76	3.14	1.84
Diethylamine	0.707	104.23	1.31	1.66	1.29	0.470
Dimethylformamide	0.944	77.37	0.031	0.110	0.270	4.54
Formamide	1.134	39.89	0.021	0.064	0.240	0.150
N-Methyl-2-pyrrolidone	1.026	96.70	0.073	0.220	2.69	8.46
2-Pyrrolidone	1.120	76.83	0.057	0.160	0.410	3.23
N,N-Dimethylacetamide	0.937	93.03	0.053	0.130	2.34	5.81
Acetone	0.791	73.93	0.056	0.150	0.370	1.73
Methyl ethyl ketone	0.805	90.20	0.120	0.420	1.11	2.63
3-Pentanone	0.853	106.40	0.240	1.15	2.03	2.67
Cyclohexanone	0.947	104.14	0.310	2.05	4.01	5.39
Methyl acetate	0.932	79.89	0.100	0.260	0.540	1.49
Ethyl acetate	0.894	98.54	0.160	0.600	0.850	1.41
Ethyl formate	0.917	80.83	0.110	0.290	0.480	3.05
Diethyl carbonate	0.975	122.40	0.160	0.640	1.07	1.12
Tetrahydrofuran	0.880	82.44	1.96	3.07	3.81	3.73
Dioxane	1.034	86.13	0.210	1.34	2.88	2.79
Ethyl ether	0.708	105.50	0.450	0.950	0.580	0.270
Nitrobenzene	1.204	103.14	0.120	0.990	3.23	5.79
Nitromethane	1.127	54.40	0.015	0.034	0.100	1.61
2-Nitropropane	0.992	91.08	0.063	0.250	0.720	3.66
Nitroethane	1.045	72.00	0.030	0.093	0.290	3.40
Butyraldehyde	0.817	90.47	0.190	0.870	2.03	3.16
Benzaldehyde	1.044	102.01	0.150	1.03	4.43	5.40
Furfural	1.160	83.16	0.049	0.091	0.480	4.86
2-Methoxyethanol	0.965	79.29	0.017	0.054	0.160	0.960
2-Butoxyethanol	0.903	131.84	0.068	0.260	0.540	0.500
2-Ethoxyethanol	0.930	97.46	0.026	0.100	0.310	0.680
2-(2-Methoxyethoxy)ethanol	1.010	118.17	0.019	0.064	0.290	1.27
Acetonitrile	0.786	52.68	0.015	0.026	0.100	0.830
Propionitrile	0.772	70.86	0.020	0.060	0.220	1.72
Butyronitrile	0.794	87.90	0.038	0.150	0.440	2.40
Benzonitrile	1.010	103.03	0.100	1.04	2.56	5.53
Methylene chloride	1.326	64.43	1.14	3.42	3.15	6.51
Chloroform	1.473	80.66	3.72	5.26	5.69	9.41
Carbon tetrachloride	1.594	97.15	5.04	6.88	4.92	1.08
1,2-Dichloroethane	1.256	79.44	0.400	1.95	3.05	6.46
1,1,1-Trichloroethane	1.338	100.28	3.91	4.68	4.07	2.24
Perchloroethylene	1.623	102.81	6.34	7.16	5.30	0.760
Trichloroethylene	1.462	90.13	5.42	6.15	5.06	3.53
Methanol	0.791	40.70	0.012	0.030	0.170	0.220
1-Propanol	0.802	74.94	0.017	0.077	0.094	0.270
1-Butanol	0.810	91.94	0.023	0.110	0.110	0.290
Ethanol	0.785	58.52	0.009	0.036	0.080	0.240

[a] Solvent densities and molar volumes obtained from Refs. 36–39.

solvent uptake volume (ϕ_1/ϕ_2, $z = 0$); the product of the fractional uptake volume and the square-root of the solvent molar volume [$(\phi_1/\phi_2)V_1^{1/2}$, $z = 0.5$]; and the product of the fractional uptake volume and the solvent molar volume [$(\phi_1/\phi_2)V_1$, $z = 1$]. Results are presented in Table II. Although using fractional weight gain yields 3DSP values similar to those obtained using fractional volume gain, expressing the uptake in terms of the latter is more consistent with eqs. (2)–(5) which relate solubility to the 3DSPs. Incorporating $V_1^{1/2}$ into the weighting factor had little effect on the δ_d values, but consistently reduced δ_p and δ_h by 0.1–0.2 MPa$^{1/2}$ compared to using ϕ_1/ϕ_2 alone. These were further reduced by 0.1–0.2 MPa$^{1/2}$ upon substituting V_1 for $V_1^{1/2}$. Overall, the butyl rubber 3DSPs showed the greatest, and nitrile the least, dependence upon the weighting factor employed. The reason for the decreasing trend in all the 3DSP values is not clear.

It is difficult to make a general statement about the importance of small changes in 3DSP values on the accuracy of estimating solubility using eqs. (2)–(5) because the effect depends on the value of A. For a solvent–polymer pair that has a large A value, which generally indicates lower mutual solubility, the effect of a small change in the polymer 3DSP on the modeled solubility will be negligible. In contrast, for small values of A, the dependence of the solubility estimate on the 3DSP value is quite important. This was illustrated in a previous general analysis of this modeling approach for a range of assumed solvent molar volumes and polymer cross-link densities.[12] It was also shown that solvents with lower molar volumes will not only be more soluble in a polymer, but will also show a greater dependence on A, all other things being equal.

In Table III, polymer 3DSP values calculated by eq. (6) using a weighting factor of $(\phi_1/\phi_2)V_1$ are compared to the 3DSPs determined by the graphical method. The range of graphical values presented is that obtained for uptake criteria ranging from 10 to 50%.[6] For δ_d, the weighted-average values are all within the ranges of the corresponding graphical values. Differences among the δ_p and δ_h values, however, are more substantial: Those determined by weighted average are consistently lower than the average graphical values, and most are outside of the ranges of graphical values.

To explore the effect of reducing the number of solvents on the 3DSP estimates obtained with the weighted-average method, the polymer 3DSPs were recalculated using subsets of $n = 40$, 27, and 13 solvents. For each n, six different determinations were made using different groups of solvents. The solvents

in each group were selected using a stratified random approach so that at least one solvent from each of the 13 chemical classes in the data set was included in each calculation.

The results are presented in Table IV along with the values obtained using all 53 solvents. As expected, the variability in a given 3DSP estimate increases as the number of solvents decreases, but the difference between the average subset-derived value and the value derived with the full data set is, in most cases, not statistically significant. The 3DSPs based on $n = 40$ differ by less than 0.1 MPa$^{1/2}$ from those derived using the full data set, and most of the relative standard deviations (rsd) are <5%. For $n = 27$ or 13, most of the 3DSPs are still very close to those determined with $n = 53$, but differences of 0.3–0.4 MPa$^{1/2}$ in δ_p and δ_h are seen for natural and neoprene and several of the rsd values are >10%. Thus, the dependence on sample size is not critical, particularly for nitrile, but a minimum of 27 solvents appears necessary to maintain reasonable precision and accuracy. This is somewhat fewer than the minimum of 42 solvents recommended by Hansen for the graphical determination method.[19]

Solubility Estimates from 3DSP Values Determined by the Weighted-average Method

The weighted-average 3DSP values ($n = 53$) were then used in eqs. (2) and (3) to determine the b weighting factors for each solvent–polymer combination (assuming $a = 1$ and $\chi_s = 0$). These calculations employed χ values obtained from experimental ϕ_1 data via eq. (5). The χ values vary inversely with S and range from 0.211 to 3.53 for this data set. Those for butyl rubber, which cover the widest range of the four polymers tested, are included in Table V.

As shown in Table V, there are many cases where solvents from the same chemical class have similar individual b values for a specific glove polymer, despite significant differences in solubility. For the solvents in the alcohol and glycol–ether classes, the b values remain similar regardless of the polymer. In such cases, using a single "group" b value for all members of the class leads to relatively little error in estimating solubility in a specific polymer. This suggests that the solubilities of untested solvents from the same classes might also be accurately estimated using the same b values.

In many cases, it was necessary to subdivide solvents from a class into smaller groups. For example, the individual b values for the amides showed a natural division based on the presence or absence of N-

Table II   Influence of Different Weighting Factors on Polymer 3DSP Values Obtained Using the Weighted-Average Method[a]

Weighting Factor	Butyl			Natural			Neoprene			Nitrile		
	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h
w_1/w_2	17.4	2.8	3.1	17.5	3.5	3.7	17.6	5.2	4.9	17.4	8.4	6.2
ϕ_1/ϕ_2	17.2	2.4	2.9	17.3	3.3	3.7	17.4	5.2	5.0	17.3	8.5	6.4
$(\phi_1/\phi_2)V_1^{l/2}$	17.1	2.2	2.8	17.3	3.1	3.5	17.5	5.0	4.9	17.3	8.3	6.3
$(\phi_1/\phi_2)V_1$	17.1	2.1	2.6	17.2	2.9	3.4	17.5	4.8	4.7	17.3	8.2	6.2

[a] Units of all δ are MPa$^{1/2}$; w_1/w_2 and ϕ_1/ϕ_2 are the fractional solvent uptake in terms of weight and volume, respectively.

methyl groups, and the cyclohexanone b values were consistently different from those of the straight-chain ketones.

Table V also shows that trends within classes are not always consistent across the four glove materials. The division of aliphatics into cyclic and straight-chain groups is justified by the individual b values for both butyl and natural rubber gloves, but not for neoprene or nitrile. In other cases, the b value for one solvent from a class is an apparent outlier for one glove material but not for the others. In several of the solvent classes (e.g., chlorinated hydrocarbons, ethers, aldehydes), a rather wide range of individual b values is obtained and there is no obvious structural rationale for subdividing the solvents.

Notwithstanding the anomalies just noted, solvents were placed into groups and assigned a group b value for the purpose of estimating solubility. In all cases, the group b value was determined by minimizing the overall error among modeled and experimental S values within the group. Since b is not linearly related to solubility, this was typically not the arithmetic average. The final groupings are indicated in Table V by those solvents sharing a common group b value. Most values are less than unity, in keeping with other reports[5,12,14,18,20-23]; however, there are a few cases with each glove type where b > 1. Mesitylene, cyclohexanone, and diethyl carbonate were treated individually, in part for structural reasons, but also because their b values were significantly different from those of the other solvents in their respective classes.

While exceptional solvents are found throughout this data set, it is evident that some correlation exists between the solvent structures and the corresponding b values. The ability to reconcile solubility es-

Table III   Comparison of Polymer 3DSP Values Determined by Three Different Methods

	δ_d (MPa$^{1/2}$)	δ_p (MPa$^{1/2}$)	δ_h (MPa$^{1/2}$)
Butyl			
Graphical[a]	17.0 (16.8–17.3)	3.5 (3.1–4.3)	3.6 (3.4–3.7)
Weighted average[b]	17.1	2.1	2.6
Regression	18.4	−5.0	−0.8
Natural			
Graphical[a]	17.0 (16.7–17.3)	6.0 (4.1–8.6)	5.2 (3.5–6.8)
Weighted average[b]	17.2	2.9	3.4
Regression	18.4	−3.7	1.4
Neoprene			
Graphical[a]	17.0 (16.3–17.3)	9.3 (6.3–13.0)	7.6 (6.1–10.3)
Weighted average[b]	17.5	4.8	4.7
Regression	19.4	3.6	4.2
Nitrile			
Graphical[a]	16.9 (16.8–17.1)	9.7 (8.9–11.3)	8.6 (7.2–10.5)
Weighted average[b]	17.3	8.2	6.2
Regression	18.9	8.6	6.0

[a] Average of 3DSPs determined graphically using 10, 25, and 50% solvent uptake criteria (range of values is presented in parentheses).
[b] Weighting factor = $(\phi_1/\phi_2)V_1$.

Table IV Effect of the Number of Solvents on the 3DSP Estimates Obtained with Both Methods

	Weighted-average Method[b]			Regression Method[b]			
n	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	b
Butyl							
Full[a]	17.1	2.1	2.6	18.4 [0.03]	−5.0 [−0.26]	−0.8 [−2.0]	0.16 [0.15]
40	17.2 (0.006)	2.0 (0.11)	2.5 (0.04)	18.3 (0.02)	−4.7 (−0.17)	−0.2 (−4.5)	0.17 (0.12)
27	17.3 (0.001)	2.0 (0.18)	2.5 (0.11)	18.2 (0.02)	−4.1 (−0.37)	−0.3 (−8.3)	0.20 (0.31)
13	16.9 (0.03)	2.4 (0.33)	2.9 (0.14)	18.3 (0.06)	−2.2 (−1.3)	−0.3 (−18)	0.24 (0.44)
Natural							
Full[a]	17.2	2.9	3.4	18.4 [0.02]	−3.7 [−0.35]	1.4 [1.0]	0.13 [0.16]
40	17.3 (0.003)	2.8 (0.06)	3.3 (0.04)	18.7 (0.03)	−3.5 (−0.35)	1.0 (0.88)	0.13 (0.16)
27	17.5 (0.005)	2.8 (0.13)	3.1 (0.10)	18.2 (0.09)	−2.7 (−0.68)	1.9 (1.1)	0.16 (0.37)
13	17.1 (0.01)	3.3 (0.17)	3.8 (0.14)	18.1 (0.03)	−1.1 (−3.0)	1.4 (3.2)	0.19 (0.51)
Neoprene							
Full[a]	17.5	4.8	4.7	19.5 [0.01]	3.6 [0.23]	4.2 [0.20]	0.18 [0.15]
40	17.4 (0.007)	4.8 (0.05)	4.7 (0.02)	19.4 (0.04)	3.5 (0.17)	3.6 (0.39)	0.16 (0.32)
27	17.6 (0.01)	4.6 (0.08)	4.3 (0.07)	19.0 (0.14)	3.2 (0.43)	2.3 (1.5)	0.18 (0.39)
13	17.4 (0.02)	5.0 (0.15)	5.0 (0.06)	18.7 (0.04)	3.0 (1.7)	2.0 (2.2)	0.19 (0.50)
Nitrile							
Full[a]	17.3	8.2	6.2	18.9 [0.01]	8.6 [0.04]	6.0 [0.07]	0.20 [0.05]
40	17.3 (0.01)	8.3 (0.02)	6.3 (0.03)	18.9 (0.01)	8.6 (0.02)	6.0 (0.02)	0.20 (0.01)
27	17.5 (0.01)	8.1 (0.06)	6.1 (0.02)	18.6 (0.02)	11.3 (0.41)	3.5 (1.3)	0.15 (0.45)
13	17.3 (0.04)	7.8 (0.08)	6.1 (0.09)	18.5 (0.04)	10.3 (0.25)	4.6 (0.46)	0.16 (0.22)

[a] $n = 53$ for the weighted-average method and $n = 48$ for the regression method. Values in brackets are relative standard errors from the regression analysis.

[b] Values in parentheses are relative standard deviations determined from six trials at each level of n.

timates with one group b value for solvents having such different polymer solubilities lends support to the notion that b is more than a mere correction factor. Unfortunately, attempts to correlate b values with various other solvent physical properties for the purpose of predicting b for untested solvents have thus far been unsuccessful.

For each solvent–polymer pair, the group b value in Table V was used in eqs. (2) and (3) to determine X_m, which, in turn, was used to determine a modeled ϕ_1 via eq. (5). The resulting modeled solubility, S_m, is given in Table V along with the ratio of the modeled-to-experimental solubility (S_m/S_e). The geometric mean of the ratios, shown in Table VI, ranges from 1.07 to 1.18 among the four polymers, indicating a slight tendency toward overestimation. But the geometric standard deviation is <2 in each case, which indicates a low overall level of variability. Linear regression of log S_m onto log S_e for the four sets of data yielded slopes of 1.00 to 1.06 and correlation coefficients (r^2) of 0.845–0.940.

For butyl and natural rubber, the ethers and aldehydes are the least accurately modeled, while for neoprene and nitrile rubber, the esters are more problematic. For nitrile, the amines also are not ac-

curately modeled. For all four gloves, there are exceptional solvents from the chlorinated hydrocarbon class. In fact, the perchloroethylene–nitrile combination represents the largest error in the data set. However, it must be recognized that the variation in the number and pattern of chlorine substituents among the members of this group results in considerable variation in polarity, polarizability, and solvent behavior. Thus, encountering a few exceptional solvents is not too surprising.

Table VI also summarizes the results in terms of the percentage of solvents having S_m values within a factor of two or three of S_e. By these criteria, the best correlations are for natural rubber with 96% (48/50) of the estimates within a factor of two and 100% within a factor of three of the actual values. Butyl gives the poorest results with 82 and 92% of the estimates within a factor of two and three, respectively. Overall, 83% (176/212) of the modeled solubilities are within a factor of two of the experimental values.

Table VI shows similar summary statistics for the case where the graphically determined values (10% uptake criterion) were used in place of the weighted-average determined 3DSPs. A separate set

Table V   Modeled Solubilities Based on 3DSPS Determined Using the Weighted-Average Method[a]

Solvent	Butyl					Natural			
	χ	b_i	b_g	S_m	S_m/S_e	b	b_g	S_m	S_m/S_e
n-Hexane	0.575	0.538	0.517	1.33	1.05	0.275	0.268	1.16	1.03
n-Heptane	0.524	0.500	0.517	1.48	0.95	0.263	0.268	1.30	0.97
Cyclohexane	0.434	0.876	0.717	3.72	1.28	0.477	0.380	3.19	1.28
Methylcyclohexane	0.411	0.603	0.717	2.24	0.79	0.310	0.380	1.97	0.79
Benzene	0.662	3.49	4.33	0.69	0.56	1.08	1.35	1.84	0.65
Toluene	0.554	14.2	4.33	6.06	3.08	1.97	1.35	4.23	1.32
o-Xylene	0.498	6.64	4.33	4.28	1.73	1.91	1.35	4.12	1.27
Mesitylene	0.459	0.872	0.872	2.58	1.00	0.307	0.307	3.23	1.00
Triethylamine	0.497	1.53	0.554	4.24	2.26	0.613	0.570	2.15	1.09
n-Butylamine	0.697	0.477	0.554	0.59	0.66	0.507	0.570	1.37	0.78
Diethylamine	0.598	0.763	0.554	2.16	1.65	0.918	0.570	2.47	1.49
Formamide	3.155	0.231	0.227	0.02	1.06	0.175	0.172	0.07	1.05
2-Pyrrolidone	2.278	0.220	0.227	0.05	0.92	0.166	0.172	0.15	0.92
Dimethylformamide	2.632	0.400	0.402	0.03	0.99	0.305	0.325	0.09	0.85
N-Methyl-2-pyrrolidone	2.025	0.408	0.402	0.08	1.04	0.323	0.325	0.22	0.99
N,N-Dimethylacetamide	2.198	0.400	0.402	0.05	0.98	0.345	0.325	0.15	0.17
Acetone	2.040	0.746	0.754	0.05	0.97	0.642	0.618	0.16	1.09
Methyl ethyl ketone	1.551	0.769	0.754	0.12	1.05	0.601	0.618	0.39	0.93
3-Pentanone	1.197	0.755	0.754	0.24	1.00	0.553	0.618	0.88	0.77
Cyclohexanone	1.124	1.10	1.10	0.31	1.00	0.859	0.859	2.05	1.00
Methyl acetate	1.742	1.01	0.829	0.16	1.61	0.943	0.721	0.49	1.86
Ethyl acetate	1.429	1.09	0.829	0.31	1.92	0.954	0.721	1.18	1.98
Ethyl formate	1.694	0.673	0.829	0.06	0.58	0.582	0.721	0.17	0.61
Diethyl carbonate	1.468	2.22	2.22	0.16	1.00	2.28	2.28	0.64	1.00
Tetrahydrofuran	0.575	0.408	0.727	0.37	0.19	0.456	0.613	1.59	0.52
Dioxane	1.357	1.53	0.727	1.19	5.63	0.930	0.613	3.09	2.30
Ethyl ether	0.865	1.97	0.727	2.05	4.50	2.75	0.613	2.61	2.74
Nitrobenzene	1.797	0.781	0.542	0.25	2.07	0.332	0.428	0.65	0.66
Nitromethane	3.412	0.539	0.542	0.01	0.98	0.473	0.428	0.05	1.36
2-Nitropropane	2.109	0.553	0.542	0.07	1.06	0.382	0.428	0.19	0.76
Nitroethane	2.756	0.511	0.542	0.02	0.83	0.393	0.428	0.07	0.79
Butyraldehyde	1.301	1.01	0.462	0.94	5.06	0.712	0.395	2.21	2.54
Benzaldehyde	1.553	0.917	0.462	0.62	4.12	0.539	0.395	1.85	1.78
Furfural	2.430	0.412	0.462	0.03	0.71	0.383	0.395	0.08	0.92
2-Methoxyethanol	3.181	0.409	0.408	0.02	1.01	0.325	0.315	0.06	1.09
2-Butoxyethanol	1.980	0.353	0.408	0.05	0.67	0.249	0.315	0.15	0.57
2-Ethoxyethanol	2.786	0.374	0.408	0.02	0.75	0.275	0.315	0.07	0.70
2-(2-Methoxy-ethoxy)ethanol	3.089	0.499	0.408	0.04	1.93	0.412	0.315	0.13	02.01
Acetonitrile	3.132	0.543	0.583	0.01	0.78	0.510	0.474	0.03	1.24
Propionitrile	2.822	0.607	0.583	0.02	1.13	0.485	0.474	0.06	1.06
Butyronitrile	2.333	0.556	0.583	0.03	0.87	0.380	0.474	0.09	0.60
Benzonitrile	1.767	0.882	0.583	0.30	2.85	0.462	0.474	0.97	0.93

(Continued)

Table V (*Continued*)

Solvent	Butyl					Natural			
	χ	b_i	b_g	S_m	S_m/S_e	b	b_g	S_m	S_m/S_e
Methylene chloride	0.790	0.976	0.929	1.31	1.15	1.05	0.758	6.27	1.83
Chloroform	0.553	1.55	0.929	8.89	2.39	2.48	0.758	10.88	2.07
Carbon tetrachloride	0.490	1.43	0.929	8.86	1.76	0.525	0.758	4.18	0.61
1,2-Dichloroethane	1.134	1.05	0.929	0.53	1.31	0.795	0.758	2.18	1.12
1,1,1-Trichloroethane	0.504	2.38	0.929	9.61	2.46	2.57	0.758	8.83	1.89
Perchloroethylene	0.430	0.347	0.929	0.94	0.15	0.351	0.758	3.34	0.47
Trichloroethylene	0.461	1.43	0.929	8.86	1.64	2.64	0.758	10.37	1.69
Methanol	3.337	0.405	0.414	0.01	0.92	0.334	0.306	0.04	1.30
1-Propanol	2.996	0.406	0.414	0.02	0.93	0.278	0.306	0.06	0.78
1-Butanol	2.749	0.389	0.414	0.02	0.82	0.252	0.306	0.07	0.61
Ethanol	3.534	0.452	0.414	0.01	1.38	0.338	0.306	0.05	1.34

Solvent	Neoprene				Nitrile			
	b_i	b_g	S_m	S_m/S_e	b_i	b_g	S_m	S_m/S_e
n-Hexane	0.308	0.304	0.23	1.02	0.254	0.253	0.07	1.01
n-Heptane	0.301	0.304	0.22	0.98	0.252	0.253	0.06	0.99
Cyclohexane	0.332	0.289	1.25	1.40	0.301	0.273	0.18	1.27
Methylcyclohexane	0.259	0.289	0.58	0.78	0.253	0.273	0.10	0.83
Benzene	0.376	0.397	2.59	0.92	0.177	0.197	1.26	0.76
Toluene	0.471	0.397	3.45	1.16	0.216	0.197	1.71	1.26
o-Xylene	0.362	0.397	3.29	0.92	0.202	0.197	1.42	1.06
Mesitylene	0.114	0.114	3.34	0.99	0.131	0.131	0.74	1.00
Triethylamine	0.343	0.371	0.74	0.82	0.223	0.245	0.18	0.22
n-Butylamine	0.599	0.371	3.87	1.23	0.690	0.245	4.39	2.38
Diethylamine	0.827	0.371	2.28	1.77	0.411	0.245	1.18	2.50
Formamide	0.126	0.133	0.21	0.88	0.206	0.190	0.18	1.23
2-Pyrrolidone	0.152	0.133	0.56	1.37	0.108	0.190	0.93	0.29
Dimethylformamide	0.211	0.197	0.87	1.21	0.209	0.182	5.17	1.14
N-Methyl-2-pyrrolidone	0.196	0.197	2.64	0.98	−0.025	0.182	6.94	0.82
N,N-Dimethylacetamide	0.172	0.197	1.74	0.74	0.200	0.182	5.99	1.03
Acetone	0.778	0.823	0.33	0.88	2.88	3.26	1.29	0.74
Methyl ethyl ketone	0.874	0.823	1.27	1.14	5.88	3.26	4.41	1.68
3-Pentanone	1.12	0.823	2.82	1.38	3.11	3.26	2.51	0.94
Cyclohexanone	3.10	3.079	3.97	1.00	1.03	1.03	5.38	1.00
Methyl acetate	1.68	1.17	1.24	2.29	5.49	1.75	5.62	3.76
Ethyl acetate	2.40	1.17	2.94	3.44	1.42	1.75	0.84	0.60
Ethyl formate	0.918	1.17	0.28	0.59	2.27	1.75	4.08	1.34
Diethyl carbonate	2.70	2.70	1.07	1.00	0.512	0.512	1.12	1.00
Tetrahydrofuran	0.891	0.863	3.89	1.02	1.23	0.424	6.62	1.77
Dioxane	0.721	0.863	2.04	0.71	0.278	0.424	1.08	0.39
Ethyl ether	2.47	0.863	1.55	2.69	0.576	0.424	0.45	1.67
Nitrobenzene	0.344	0.392	2.87	0.89	−0.008	0.268	5.07	0.88
Nitromethane	0.427	0.392	0.12	1.25	0.248	0.268	1.28	0.80
2-Nitropropane	0.383	0.392	0.68	0.94	0.523	0.268	5.92	1.62
Nitroethane	0.339	0.392	0.21	0.71	0.268	0.268	3.38	1.00

(*Continued*)

Table V (*Continued*)

Solvent	Neoprene				Nitrile			
	b_i	b_g	S_m	S_m/S_e	b_i	b_g	S_m	S_m/S_e
Butyraldehyde	1.10	0.290	3.48	1.72	0.491	0.235	4.03	1.28
Benzaldehyde	0.590	0.290	5.30	1.20	1.52	0.235	6.27	1.16
Furfural	0.285	0.290	0.46	0.96	0.221	0.235	4.53	0.93
2-Methoxyethanol	0.280	0.272	0.18	1.08	0.209	0.270	0.49	0.51
2-Butoxyethanol	0.252	0.272	0.46	0.84	0.334	0.270	0.83	1.66
2-Ethoxyethanol	0.238	0.272	0.23	0.73	0.295	0.270	0.84	1.25
2-(2-Methoxy-ethoxy)ethanol	0.328	0.272	0.45	1.54	0.305	0.270	1.67	1.32
Acetonitrile	0.416	0.407	0.10	1.05	0.319	0.361	0.60	0.72
Propionitrile	0.402	0.407	0.21	0.97	0.420	0.361	2.34	1.36
Butyronitrile	0.358	0.407	0.34	0.76	0.506	0.361	3.38	1.41
Benzonitrile	0.598	0.407	4.10	1.60	0.642	0.361	6.66	1.20
Methylene chloride	4.92	0.429	11.94	3.79	3.97	0.281	13.37	2.50
Chloroform	3.18	0.429	11.53	2.03	0.273	0.281	9.28	0.99
Carbon tetrachloride	0.280	0.429	1.93	0.39	0.215	0.281	0.55	0.51
1,2-Dichloroethane	2.00	0.429	8.39	2.75	1.52	0.281	9.74	1.51
1,1,1-Trichloroethane	1.38	0.429	7.95	1.95	0.447	0.281	5.27	2.36
Perchloroethylene	1.26	0.429	8.69	1.64	1.48	0.281	8.20	10.75
Trichloroethylene	3.47	0.429	10.62	2.10	0.526	0.281	7.82	2.21
Methanol	0.204	0.282	0.08	0.46	0.249	0.266	0.19	0.86
1-Propanol	0.319	0.282	0.13	1.38	0.275	0.266	0.29	1.08
1-Butanol	0.331	0.282	0.16	1.46	0.280	0.266	0.32	1.13
Ethanol	0.312	0.282	0.10	1.28	0.267	0.266	0.24	1.01

[a] Units of S_m and S_e are g/mL; b_i and b_g are the individual and group weighting factors, respectively (see text).

Table VI   Geometric Mean and Geometric Standard Deviation of S_m/S_e and the Number of Solvents Whose S_m Values Fall Within a Factor of Two (2×) or Three (3×) of S_e (n = 53) for Polymer 3DSPs Determined by Each Method

	Geometric Mean S_m/S_e	Geometric SD S_m/S_e	2×	3×
Butyl				
Graphical[a]	1.41	2.51	36	43
Weighted average	1.18	1.96	41	46
Regression	0.996	2.45	31	43
Natural				
Graphical[a]	1.40	2.45	34	43
Weighted average	1.07	1.53	48	53
Regression	0.997	2.17	35	47
Neoprene				
Graphical[a]	1.59	3.81	27	35
Weighted average	1.17	1.59	44	51
Regression	1.10	2.05	35	46
Nitrile				
Graphical[a]	1.18	2.08	40	45
Weighted average	1.13	1.83	43	49
Regression	1.09	1.81	45	50

[a] 3DSPs determined using a 10% uptake criterion (see Ref. 6).

of b values was calculated using the same solvent groups as in Table V, again by minimizing groupwise errors in S_m. As shown, the correlations are consistently weaker using the graphical 3DSPs. The geometric mean ratios of S_m/S_e range from 1.18 to 1.59 and the geometric standard deviations are all >2. The best overall results are for nitrile, but only 80% of the solubility estimates are within a factor of two of the experimental values. Several of the estimates are off by a factor of 20 or more. Thus, use of the weighted-average method for determining polymer 3DSPs appears to have tangible advantages over the graphical method for this approach for estimating solvent uptake.

3DSP Values Determined by the Multiple Regression Method

During initial attempts to determine polymer 3DSPs by multiple regression, the following five solvents emerged as outliers in three of the four glove analyses (nitrile was the exception): acetonitrile, formamide, nitromethane, methanol, and ethanol. The residual errors, $(X - X_m) RT/V_1$, for these solvents were significantly larger than for the remaining solvents. Residual errors for 2-pyrrolidone were also large for the butyl and natural rubber analyses. For the nitrile glove, errors were the largest for perchloroethylene, methylene chloride, and butyraldehyde, but these were small compared to those for the five outliers identified with the other gloves.

The five exceptional solvents have the lowest molar volumes of all the solvents studied ($V_1 < 60$ cm³/mol). They are also among the solvents with the lowest solubilities and, consequently, the largest X values, in each polymer. 2-Pyrrolidone has these same attributes. Solvents with low molar volumes that are more soluble in the polymers, or solvents with higher molar volumes but low solubilities, are well behaved. Thus, it appears that both conditions are required to produce a poor fit to the model. Hansen noted difficulty modeling solvents with low molar volumes using solubility parameters, as mentioned above.[31,32] The complementary condition of low solubility has not been noted previously.

For the purposes of estimating the polymer 3DSPs, these outliers were omitted and the regression analyses for all of the glove polymers were based on the remaining 48 solvents. Table III presents the 3DSP values obtained. The δ_d values for all four polymers are significantly greater than those determined by the two other methods, and they are outside the ranges of the graphical δ_d values. Although the δ_p and δ_h values for neoprene and nitrile are similar to those obtained by the weighted-average method, the δ_p values for butyl and natural rubber and the δ_h value for butyl rubber are negative.

Theoretically, solubility parameters cannot be negative, at least as far as they were defined by Hildebrand et al. for volatile solvents.[15] However, if it is accepted that polymer 3DSPs are merely sets of empirical parameters used to characterize the interactions affecting solvent–polymer solubility, there should be no particular objection to negative values. Beerbower and Dickey reported a δ_p value of -3.9 for natural rubber on the basis of a different type of regression analysis.[5] They rationalized the negative value on the basis of the 3DSPs being mathematical tools for establishing meaningful correlations rather than thermodynamic constants.

For butyl and natural rubber, the δ_h value is expected to be close to zero. Our value of $\delta_h = -0.8$ MPa$^{1/2}$ for butyl rubber is not statistically different from zero at the 95% confidence level. This is also true for our natural rubber δ_h value of 1.4 MPa$^{1/2}$.

The multiple-regression correlation coefficients (R^2) ranged from 0.910 to 0.960 and the relative standard errors were small for δ_d (1–3%), δ_p (4–35%), and b (5–16%) for all four polymers, as well as for δ_h for neoprene and nitrile (7–20%). The estimates of δ_h for butyl and natural rubber, however, were significantly less precise (see Table IV). The estimates of all variables for nitrile stand out as having the least residual error. The regression analysis yielded b weighting factors of 0.16, 0.13, 0.18, and 0.20 for butyl, natural, neoprene, and nitrile, respectively, which are similar to those reported by other investigators for analogous correlations in various solvent–solvent and solvent–polymer systems.[5,12,21,22]

If it can be assumed that the difference between X and X_m is attributable to X_s, a correlation might be expected between X_s (or X_s/X) and the structures of the solvents. X_s ranged in magnitude from 0.01 to 1.15, and both positive and negative X_s values were found, which runs contrary to its being defined as an entropic (i.e., positive) correction term. In most cases, $0.1 < |X_s/X| < 0.40$, but for each glove at least 10 solvents gave $|X_s/X| > 0.50$, and in two cases (i.e., perchloroethylene–butyl and 2-pyrrolidone–nitrile), $X_s > X$. The magnitude of X_s/X, however, did not always correlate with the degree of error in S_m (see below), in part, because S_m depends on the magnitude of both X and X_s/X, i.e., the dependence of S_m on X is weaker at higher values of X. No trends were found to suggest a relationship between the structure or class of a solvent and the values of X_s or X_s/X in any of the glove polymers.

The effect of reducing the number of solvents in the data set on the regression-based 3DSPs is shown in Table VII. As with the weighted-average method, six trials were run for each subset of n solvents using a stratified random solvent selection procedure. In general, the variability around the parameters determined using the regression method is greater than that with the weighted-average method. This is particularly marked for the butyl and natural rubber estimates of δ_p and δ_h as indicated by several of the rsd values being greater than unity. Even for nitrile, variations in the δ_p and δ_h values are very high for $n \leq 27$. In contrast, the b values are relatively insensitive to n. Overall, the butyl and natural rubber 3DSP values are the least precise and the most affected by n, followed in order by those for neoprene and nitrile.

Solubility Estimates from 3DSP Values Determined by Regression

Table VII presents S_m and S_m/S_e determined for each solvent–polymer pair with the regression-derived 3DSPs. Summary data are presented in Table VI. The advantage in terms of generality imparted to the regression method by using a single b weighting factor for all solvents in a given polymer, rather than group-specific b values as in the preceding approach, must be recognized. However, the accuracy with which the solvent–polymer solubilities are estimated is somewhat lower overall as a result. As expected, the geometric mean S_m/S_e ratios are close to unity for all four gloves, but there is still a tendency toward overestimation. The range of error, as reflected in the geometric standard deviations, is generally greater than that with the weighted-average 3DSPs, but consistently less than that with the graphical 3DSPs. Linear regression of $\log S_m$ vs. $\log S_e$ gave slopes of 0.83–1.06 and r^2 values of 0.775–0.845. Once again, the results for nitrile are the best.

Not surprisingly, the solubility estimates for the five outlier solvents identified above are not very accurate in the butyl, natural, and neoprene polymers. However, several other solvents have larger discrepancies between S_m and S_e. Reviewing the data by chemical class reveals a few error trends, but nothing that would suggest the model to be inappropriate. For example, the S_m values for the aromatic solvents are consistently high in three of the four gloves, but the range of errors is not excessive. The amides tend to be underestimated and the esters tend to be overestimated in all of the polymers, but, again, the errors are typically small. Note also that none of the amines are modeled very well in the first

three polymers and that the results for the 1° and 2° amines differ from those of the 3° amine. No other trends are apparent.

In terms of the percentages of S_m within a factor of two or three of S_e, the results are mixed. For butyl and natural rubbers, the regression-based values provide solubility estimates of comparable accuracy to those obtained with the graphical 3DSPs, while for the other two glove polymers, the regression-based values yield a much greater fraction of accurate estimates. Overall, using the regression-based 3DSPs provides 69 and 88% of the modeled solubilities within a factor of two and three of the experimental values, respectively. For nitrile, 85% are within a factor of two and 94% are within a factor of three.

Solvents for which S_m and S_e differ by more than a factor of three are distributed throughout the classes of chemicals represented in the data set. Diethylamine and nitromethane are outliers for three of the four gloves, and dioxane, perchloroethylene, and butyraldehyde are outliers for two gloves. The latter three solvents were also among the less accurately modeled solvents when using the weighted-average-based 3DSPs. The diethylamine solubility is consistently underestimated, suggesting that it may be self-associating in the relatively nonpolar polymer matrices. The remaining errors are distributed fairly evenly among the more soluble and less soluble solvents across all glove polymers.

CONCLUSIONS

The two methods described here for determining 3DSPs for lightly crosslinked polymers address several of the problems associated with the standard graphical method. The first method, which employs a weighted average of immersion-test solvent 3DSPs, is conceptually and computationally straightforward, makes efficient use of all of the data collected during the immersion tests, and avoids the arbitrariness of the graphical method related to deciding on the minimum uptake criterion and defining the spherical solubility zone. In addition, each solvent 3DSP contributes to the polymer 3DSP estimate to an extent that reflects the uptake of that solvent by the polymer, which makes inherent sense. While the functional dependence of the 3DSP values on solvent uptake and molar volume assumed in this method is not rigorously consistent with the supporting theory, the inclusion of these two variables in the method, alone, represents a refinement of the graphical

Table VII   Modeled Solubilities Based on Polymer 3DSPs Determined Using the Regression Method

Solvent	Butyl		Natural		Neoprene		Nitrile	
	S_m	S_m/S_e	S_m	S_m/S_e	S_m	S_m/S_e	S_m	S_m/S_e
n-Hexane	0.417	0.331	0.573	0.507	0.124	0.562	0.046	0.645
n-Heptane	0.504	0.325	0.733	0.550	0.138	0.604	0.044	0.680
Cyclohexane	4.35	1.50	4.32	1.73	1.51	1.68	0.226	1.59
Methylcyclohexane	1.96	0.689	2.44	0.984	0.422	0.570	0.104	0.827
Benzene	6.81	5.45	6.81	2.41	5.58	1.97	1.17	0.705
Toluene	4.23	2.15	5.28	1.65	4.84	1.63	1.31	0.961
o-Xylene	3.19	1.29	4.85	1.49	4.32	1.21	0.921	0.688
Mesitylene	4.48	1.74	4.70	1.45	2.59	0.766	0.225	0.303
Triethylamine	3.27	1.75	3.77	1.91	2.29	2.55	0.233	0.994
n-Butylamine	0.170	0.193	0.637	0.361	1.60	0.510	2.27	1.23
Diethylamine	0.192	0.147	0.490	0.295	0.381	0.296	0.293	0.619
Formamide	0.012	0.584	0.041	0.641	0.065	0.273	0.155	1.04
2-Pyrrolidone	0.016	0.284	0.060	0.373	0.233	0.565	1.55	0.479
Dimethylformamide	0.033	1.06	0.113	1.06	0.425	0.590	3.97	0.874
N-Methyl-2-pyrrolidone	0.048	0.658	0.165	0.749	1.24	0.462	6.88	0.813
N,N-Dimethylacetamide	0.035	0.660	0.123	0.929	0.488	0.208	4.08	0.703
Acetone	0.089	1.60	0.245	1.68	0.736	1.97	3.82	2.21
Methyl ethyl ketone	0.110	0.938	0.316	0.749	1.20	1.09	4.03	1.54
3-Pentanone	0.110	0.462	0.095	0.083	0.932	0.458	2.69	1.01
Cyclohexanone	0.297	0.963	1.34	0.652	5.28	1.32	6.50	1.21
Methyl acetate	0.166	1.65	0.489	1.87	1.33	2.46	3.89	2.60
Ethyl acetate	0.174	1.09	0.565	0.944	1.37	1.60	2.49	1.77
Ethyl formate	0.107	1.01	0.310	1.09	0.864	1.79	3.64	1.19
Diethyl carbonate	0.349	2.16	1.54	2.42	2.67	2.49	1.78	1.59
Tetrahydrofuran	0.281	0.143	1.21	0.394	3.94	1.03	5.65	1.51
Dioxane	1.45	6.87	5.23	3.894	7.38	2.56	5.09	1.82
Ethyl ether	0.153	0.337	0.335	0.351	0.265	0.461	0.230	0.859
Nitrobenzene	0.176	1.48	0.560	0.569	6.49	2.01	8.62	1.49
Nitromethane	0.055	3.60	0.142	4.13	0.311	3.24	1.55	0.964
2-Nitropropane	0.065	1.02	0.110	0.433	0.628	0.866	4.05	1.11
Nitroethane	0.051	1.72	0.139	1.492	0.374	1.28	2.65	0.780
Butyraldehyde	0.130	0.700	0.326	0.374	0.47	0.231	0.802	0.254
Benzaldehyde	0.219	1.45	0.842	0.814	6.48	1.46	8.08	1.50
Furfural	0.052	1.06	0.160	1.75	0.917	1.90	6.75	1.39
2-Methoxyethanol	0.027	1.59	0.095	1.760	0.187	1.15	0.509	0.531
2-Butoxyethanol	0.029	0.423	0.115	0.440	0.234	0.431	0.440	0.874
2-Ethoxyethanol	0.021	0.807	0.078	0.806	0.185	0.602	0.644	0.950
2-(2-methoxyethoxy)ethanol	0.024	1.21	0.093	1.45	0.240	0.814	0.837	0.661
Acetonitrile	0.044	2.99	0.110	4.22	0.234	2.44	1.20	1.45
Propionitrile	0.043	2.12	0.113	1.88	0.273	1.24	1.75	1.02
Butyronitrile	0.039	1.03	0.105	0.687	0.266	0.603	1.58	0.660
Benzonitrile	0.160	1.53	0.515	0.493	3.46	1.35	6.41	1.16
Methylene chloride	1.32	1.16	5.89	1.72	11.4	3.63	13.5	2.07
Chloroform	3.04	0.818	5.22	0.991	10.8	1.90	9.45	1.00

(*Continued*)

Table VII   *(Continued)*

Solvent	Butyl		Natural		Neoprene		Nitrile	
	S_m	S_m/S_e	S_m	S_m/S_e	S_m	S_m/S_e	S_m	S_m/S_e
Carbon tetrachloride	11.9	2.36	11.4	1.66	7.45	1.51	1.01	0.936
1,2-Dichloroethane	0.633	1.57	2.76	1.41	9.51	3.12	11.3	1.75
1,1,1-Trichloroethane	1.39	0.355	4.26	0.910	5.69	1.40	4.02	1.80
Perchloroethylene	0.684	0.108	2.82	0.394	10.5	1.99	11.0	14.4
Trichloroethylene	2.49	0.460	7.50	1.22	10.2	2.02	8.46	2.40
Methanol	0.034	2.88	0.096	3.18	0.125	0.721	0.243	1.12
1-Propanol	0.031	1.76	0.103	1.34	0.159	1.68	0.301	1.11
1-Butanol	0.028	1.20	0.100	0.869	0.158	1.48	0.282	0.988
Ethanol	0.031	3.34	0.098	2.74	0.144	1.80	0.287	1.19

method. As expected, the accuracy and precision of the 3DSP estimates gradually decline as the number of solvents used in the determination decreases, but the dependence on the size of the data set is not very critical. The insensitivity of the 3DSP values to changes in the specific solvents in the data set represents an additional improvement over the graphical estimation method.

The regression method of 3DSP determination has several of the same advantages cited for the weighted-average method. It is rigorous, it makes efficient use of all of the immersion-test data, and it affords a way to assess the precision of the 3DSP values obtained. While the computations are more involved than those used in the weighted-average method, the regression method is still far less cumbersome than is the graphical method. The availability of nonlinear regression routines in standard statistical packages makes this approach readily accessible to the nonstatistician. The integration of this method with the theories relating 3DSPs to solubility is a key attribute. Since the immediate goal is to model solubility, it is logical to derive the 3DSPs in the context of the theoretical expressions developed for that purpose.

Although the full data set used in this study consisted of 53 solvents, fewer solvents could be used for estimating the polymer 3DSPs. Results for both methods indicate that at least 27 solvents, selected to represent as wide a range of structures and functionalities as possible, are needed for reasonable accuracy and precision.

Estimating solubility using the weighted-average-based 3DSP values is limited by the need to assign b weighting factors to the various groups of solvents. As in our previous study,[12] there were apparent correlations between solvent structures and b values, but these varied with the specific polymer and there

were numerous exceptional solvents identified. While the solvent groups and associated weighting factors derived in this study provided modeled solubilities that were within a factor of two of the experimental values in the vast majority of cases, a means of assigning these weighting factors a priori is needed in order to predict solubilities for untested solvents.

In general, the solubility estimates obtained using the regression-based 3DSPs were less accurate than those obtained using the weighted-average-based 3DSPs, with the exception of those for nitrile. However, the approach to estimating solubility using the regression 3DSPs is more general because there is no need to specify b values. In addition, the accuracy achieved is sufficient for many potential applications.

The weakest correlations between modeled and experimental solubilities were for butyl rubber, regardless of the method chosen to determine the 3DSPs. Since the equations used for estimating solubility are expected to be more accurate for such a nonpolar material, the observed error may be attributable to the fairly large percentage of carbon black filler in the butyl glove formulation used here. Although the influence of the filler was accounted for in the determination of the effective crosslink density for this material, there may be additional constrictive effects on solvent uptake which cannot be addressed in the context of the theoretical expressions employed. That the best results were obtained for nitrile is also surprising, since it has the most complex structure of the polymers examined.

This is the first study to demonstrate a generally applicable 3DSP-based approach to the quantitative estimation of solvent uptake by crosslinked polymers. The capability of the approach to provide rea-

sonably accurate solubility estimates has been shown. Its extension to other solvent–polymer systems, including systems containing solvent mixtures, is currently under investigation.

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