Three-Dimensional Solubility Parameters and Chemical Protective Clothing Permeation. I. Modeling the Solubility of Organic Solvents in Viton® Gloves

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SYNOPSIS

A model based on the polymer solution theory of Flory and Rehner is presented for estimating the solubility of organic solvents in chemical protective clothing (CPC) polymers using three-dimensional (3-D) solubility parameters. Immersion test solubility values of 40 organic solvents in commercial Viton® glove samples are used to develop and assess the performance of the model. It is found that the solvent–polymer 3-D solubility parameter differences must be weighted to obtain accurate solubility estimates. However, in most cases, a single weighting factor is sufficient to bring estimated values within a factor of two of experimental values for the members of a given chemical class. The effect of temperature on solubility from 25 to 37°C is predicted within 6%, on average, for the subset of 17 solvents examined. In the companion article that follows, solubility values estimated with this approach are combined with diffusion coefficients, also estimated using 3-D solubility parameters, to determine solvent–Viton breakthrough times and steady-state permeation rates.

INTRODUCTION

Arguably, one of the most critical applications requiring knowledge of solvent–polymer interactions is the selection of polymeric chemical protective clothing (CPC) materials for individuals working with toxic chemicals. Guidance in the selection process can be obtained from CPC manufacturers' literature or other published compilations of experimental breakthrough times (BT) and steady-state permeation rates (SSPR),[1-4] but such data are available for only a limited number of solvent/CPC combinations and their interpretation is often obscured by poor documentation of experimental variables (e.g., analytical detection limits, product formulations, and temperature) and/or differences in test-system designs.[5,6] Although standard methods have been developed for CPC users to test permeation under conditions relevant to their application,[7] rarely are sufficient resources available for a thorough investigation of all the important variables influencing the barrier effectiveness in a given practical situation.

The need to develop broadly applicable CPC selection strategies for industrial hygiene applications has led to a number of reports on the use of solubility parameters to model solvent–CPC permeation.[8-17] These efforts were motivated in part by the availability of published values of simple (i.e., Hildebrand) and three-dimensional (3-D) solubility parameters for many common organic solvents and CPC polymers.[18,19] In all these reports, attempts have been made to correlate the difference between the solubility parameter(s) of the solvent(s) and CPC material directly with experimental BT and SSPR values. Although smaller solubility parameter differences were usually associated with lower permeation resistance, the correlations were typically quite weak and the predictions of BT and SSPR largely unsuccessful.[8,12,17]

The assumption underlying this approach is that the solubility parameter difference, alone, provides an accurate measure of solubility, S, and, therefore,

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should be correlated with permeability either directly, since BT and SSPR are directly proportional to S, or indirectly, since the solvent diffusion coefficient, D, is also known to vary with S. However, none of the reports employing this approach have provided an explicit relationship between S and the solubility parameter difference. The failure to account for other relevant variables such as temperature, solvent molar volume, and the degree of CPC cross-linking has undoubtedly contributed to the poor results obtained. Moreover, without a clear relationship between S and the solubility parameter difference, it is not possible to interpret such data in the context of accepted permeation theory based on Fick's laws of diffusion.

In this article and the companion article that follows, an alternative modeling approach is explored in which 3-D solubility parameters are used to obtain explicit estimates of S and D, which can then be used in Fickian diffusion equations to determine BT and SSPR. In this first paper, a focus is placed on modeling S. Well-known expressions derived from the polymer solution theories of Hildebrand et al.[20] and Flory and Rehner[21] are used as the basis for relating the 3-D solubility parameters of solvents and polymers to S. The expressions used in the model were originally developed using simple solubility parameters, and although the concept of using 3-D solubility parameters in these expressions has been discussed,[22,23] experimental studies have not been reported. Following a review of the relevant theoretical background and key simplifying assumptions of the model, its application to estimating the solubilities of various organic solvents in commercial Viton® glove samples is examined.

THEORETICAL BACKGROUND AND MODEL DEVELOPMENT

The total free-energy change accompanying dissolution of a solvent in a lightly cross-linked polymer consists of the sum of the free-energy contributions from mixing and from the elasticity of the polymer network.[24] The theory of Flory and Rehner attempts to account for these contributions in the following equilibrium expression[21,25]:

$$-RT(\ln \phi_1 + \phi_2 + \chi\phi_2^2) = 2V_1K(\phi_2^{1/3} - \phi_2/2) \quad (1)$$

where R is the gas constant (cal/mol K); ϕ_1 and ϕ_2, the volume fractions of the solvent and polymer, respectively; V_1, the solvent molar volume (cm^3/mol); K, a constant related to the low-stress modulus (cal/cm^3)[24,26,27]; and χ, the dimensionless Flory interaction parameter that, as shown below, can be estimated from the solvent and polymer solubility parameters.

Solving for χ gives

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

where $\nu = K/RT$ is the average polymer cross-link density (mol/cm^{-3} or simply cm^{-3}). It is assumed in eq. (2) that there are four segments at each point of cross-linking, the volume fraction of polymer is unity during the cross-linking process, and there is no change in free volume upon mixing.[28] For any value of χ, there will be a unique value of ϕ_1, which can be expressed in more conventional units (e.g., g/cm^3) by multiplying ϕ_1/ϕ_2 by the solvent density. Thus, if χ is known for a given solvent/polymer pair, S can be obtained.

It is now generally recognized that eq. (1) provides only an approximate model of solvent–polymer solubility, in large part because of violations of the assumption of zero excess volume change upon mixing.[29,30] However, it continues to provide a useful framework for studies of solubility interactions between solvents and polymers.[22,31,32]

Relating δ to Solubility

The simple solubility parameter, δ_S, is defined as the square root of the molar energy of vaporization per unit volume, $(\Delta E/V)^{1/2}$ and has units of $(J/cm^3)^{1/2}$.[19] The value of δ_S for a volatile solvent can be determined by measuring the heat of vaporization directly or by calculating the heat of vaporization from vapor pressure data.[33,34] For a polymer, δ_S can be estimated by immersion in a series of solvents with known δ_S values.[32,33] The polymer is assigned the δ_S value of the solvent(s) in which it most readily dissolves or in which it shows the greatest degree of swelling.

The Flory interaction parameter can be related to the solubility parameters of a pair of mixture components by

$$\chi = \chi_S + \chi_H = \chi_S + V_1(\delta_1 - \delta_2)^2/(RT) \quad (3)$$

where χ_H is the enthalpic contribution to χ, related to the solubility parameters as shown in eq. (3), and χ_S is a positive correction factor used to account for disparities between χ and χ_H where simple δ values are used.[35] Disparities have been ascribed to entropic

effects such as nonrandom orientations of the mixture components arising from specific types of chemical interactions,[29] but additional (nonentropic) factors are thought to affect the value of χ_S.[36] The lack of a definitive characterization of these factors requires that χ_S be approximated or determined experimentally.

Combining eqs. (2) and (3) provides an expression relating the solubility parameter difference, A, to the equilibrium solubility in terms of the volume fraction:

$$A^2 = (\delta_1 - \delta_2)^2 = -RT[2\nu(\phi_2^{-5/3} - \tfrac{1}{2}\phi_2^{-1}) + (\ln \phi_1/\phi_2^2\,\phi_2^{-1} + \chi_S)/V_1] \quad (4)$$

Implicit in the use of simple solubility parameters to estimate χ_H in eq. (3) is the assumption that interactions occurring between mixture components are governed solely by dispersive intermolecular forces.[35] Equation (3) is strictly applicable, therefore, only to mixtures of nonpolar or weakly polar molecules. The desire to expand the solubility parameter concept to account for additional intermolecular interactions affecting solubility has led to the development of 3-D solubility parameters where a solvent or polymer is assigned a set of parameters corresponding to each of three interaction forces: dispersion, dipole–dipole, and hydrogen-bonding (or charge transfer).[37–39] The total 3-D solubility parameter, δ_t, is represented as the sum of these solubility parameters:

$$\delta_t = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2} \quad (5)$$

where subscripts d, p, and h represent dispersion, polar (i.e., dipole–dipole), and hydrogen-bonding forces, respectively. Differences in solubility parameters between two materials are then calculated as

$$A = \delta_1 - \delta_2 = [a(\delta_{d1} - \delta_{d2})^2 + b(\delta_{p1} - \delta_{p2})^2 + b(\delta_{h1} - \delta_{h2})^2]^{1/2} \quad (6)$$

where a and b are empirical weighting factors (discussed in more detail below).[19,40] Assignment of 3-D solubility parameters to polymers is typically based on correlations established from immersion testing with solvents whose values have been determined independently.[41,42]

The value of A from eq. (6) can be used to determine χ_H in eq. (3), which, in turn, is used to solve for χ. The problem remains to determine χ_S. To use eqs. (3) and (4) in a predicitive capacity, it is necessary to assign a fixed value to this term. Setting $\chi_S = 0.34$ has been recommended when using simple solubility parameters, based on the report of Blanks and Prausnitz[43]; however, values considerably lower and higher have also been reported.[36] A value of $\chi_S = 0$ has been adopted in this model under the assumption that the use of 3-D solubility parameters, rather than simple solubility parameters, to estimate χ_H effectively accounts for the types of chemical interactions between the solvent and CPC polymer that would otherwise have to be accounted for in the χ_S term. The validity of this assumption is examined below.

Weighting Factors

A few comments about the weighting factors in eq. (6) are appropriate at this point since their importance has been overlooked in previous attempts to use 3-D solubility parameters to predict CPC permeation.[8–17] In most reports, a factor of $a = 4$ has been applied to the dispersion term of eq. (6) (and $b = 1$ assumed for the other terms) in order to render the spatial distribution of solubility parameters of solvents and polymers more symmetric when they are plotted in 3-D space. The distribution would otherwise be compressed along the δ_d axis because δ_d values do not vary as much as δ_p and δ_h between different solvents.[37] This then allows the creation of a more or less spherical "solubility zone" around a given polymer that can be characterized by a critical radius.[15,26,41] The length of the critical radius is chosen based on some arbitrary level of swelling or permeation, so that relatively soluble or permeable solvents are within the sphere and relatively less soluble solvents are outside of it. It has been implied that S is inversely proportional to the distance from the center of the sphere,[15,26,41] but this has not been demonstrated. Thus, although there is some justification for setting $a = 4$ and $b = 1$ for the purpose of roughly categorizing the relative solubilities or permeabilities of different solvents, there is no apparent justification for these particular values of a and b in the use of eq. (6) to obtain quantitative estimates of solvent–CPC solubilities.

Still, there is an apparent need for weighting factors to account for changes in the importance of the various interaction forces as a function the specific solvents and polymers under consideration. This has been documented quite clearly in studies of alcohols, glycol ethers, and carboxylic acids,[34,40,44] where the solvents tend to self-associate to an extent that depends on the solubility properties of other solvents (or polymers) that are present and on temperature.

Although most pronounced for chemicals capable of strong hydrogen-bonding interactions, similar changes in the importance of interaction forces will occur with non-hydrogen-bonding solvents as well.[19]

Hansen and Beerbower[40] recommended using factors of $a = 1$ and $b = 0.25$, rather than $a = 4$ and $b = 1$, as a rule of thumb for systems of polymers with organic solvents. Although the effect on the shape of the "solubility zone" and relative spatial distribution of solvent–polymer distances is the same in either case, the effect on the absolute solubility estimate is quite different: b values less than unity reduce the weight placed on the differences in δ_p and δ_h between two materials, rendering the total difference smaller and leading to higher solubility estimates. Values of b less than unity have been rationalized as adjustments for both the induction of dipoles in nonpolar materials by more polar materials and the variation in the probability of specific interactions occurring upon collisions between a given pair of system components.[45] Specific values of b have been published for only a few selected solvents based on solvent–solvent mixture studies.[40,45,46] It is evident from these limited data that such weighting factors will indeed vary with the structures of the interacting species and that, at present, they must be determined empirically.

Temperature Effects

In addition to the direct effect of temperature on solubility indicated in eq. (4), the molar volume of the solvent and the solubility parameters of the solvent and polymer will also change with temperature. Changes in solubility parameter values with temperature can be expressed in terms of the volume thermal expansion coefficient, α (K^{-1}).[40,47] Approximate relationships between the thermal expansion coefficients and the components of the 3-D solubility parameters are given in eqs. (7)–(9)[40]:

$$d\delta_d/dT = -1.25\alpha\delta_d \tag{7}$$

$$d\delta_p/dT = -\delta_p\alpha/2 \tag{8}$$

$$d\delta_h/dT = -\delta_h(1.22 \times 10^{-3} + \alpha/2) \tag{9}$$

As shown by these equations, the solubility parameters will decrease with increasing temperature. The effect on the solubility parameter difference between a solvent and polymer will thus depend on their respective α values.

EXPERIMENTAL

Table I lists the 40 solvents used to develop and evaluate the model for the North Viton® glove samples examined in this study along with other relevant physical properties. The 3-D solubility parameters for Viton® and for the solvents at 25°C were obtained from Refs. 12 and 18, respectively.

Immersion test weight gains at 37°C were obtained from the report of Perkins and Tippit[48] based on the work of Holcomb.[10] Additional data were obtained at both 25 and 37°C in this study by placing rectangular samples weighing from 0.5 to 0.8 g in flasks containing 30 mL of solvent and immersing the flasks in a constant-temperature water bath for 5 days. Glove samples were then removed, gently wiped clean of excess solvent, and reweighed in a sealed weighing bottle. All tests were performed in duplicate. As a quality control measure, samples were then dried in an oven at 50°C for 1–2 days, allowed to reequilibrate with atmospheric moisture at room temperature, and reweighed to estimate any loss of additives caused by solvent extraction (typically less than a few percent).

The immersion test weight gains reported by Holcomb[10] and those obtained in this study were comparable for 17 of the 20 solvents common to both data sets (mean difference < 3%), indicating that differences in the formulations of the tested Viton® samples, if any, had a small effect on solubility. For *N*-methylpyrrolidone, 3-pentanone, and 4-methyl-2-pentanone, there were significant discrepancies, probably attributable to experimental error: These solvents are among the most soluble of those tested and the samples tended to offgas quite rapidly upon removal from the solvent baths. Several additional tests were therefore performed with these solvents and the average values were used for calculating solubilities.

Experimental solubility (S_E) values were calculated assuming Viton® densities of 1.86 and 1.85 g/cm^3 at 25 and 37°C, respectively.[49] Solvent molar volumes and densities were obtained from standard references and the values at 25 and 37°C were used to estimate the volume thermal expansion coefficients. An α value of 4.8×10^{-4} K^{-1} was used for Viton® based on data from the polymer manufacturer. The degree of Viton® cross-linking was not available from the glove manufacturer. Therefore, the effect of cross-linking on solubility estimates was examined for ν values ranging from 5×10^{-5} to 5×10^{-4} cm^{-3}, which is within the range typical of lightly cross-linked polymers.[25–27]

The unweighted 3-D solubility parameter difference between Viton® and each solvent at 37°C was calculated using eq. (6) after correcting the reference solubility parameter values in Table I (25°C) using eqs. (7)–(9). The resulting value of A was used in eq. (4) to determine ϕ_1, from which the unweighted modeled solubility, $S_{Mu} = \rho_1\phi_1/\phi_2$, was then calculated using the solvent density, ρ_1 (g/cm^3), at 37°C. Weighting factors were determined for each individual solvent as described below (see Results and Discussion). Where possible, group weighting factors were also determined for the solvents within a given class and weighted modeled solubilities, S_{Mw}, were calculated using these latter values of a and b.

The accuracy of the model in accounting for the change of S with temperature was examined by comparing immersion test solubilities obtained at 25 and 37°C for a subset of 17 solvents. This temperature range is the most relevant since glove temperatures will likely be in this range for individuals working in normal indoor environments. S_E values were calculated by multiplying the fractional weight gain by the Viton® density at the appropriate temperature. Ratios of the experimental solubilities at the two temperatures were compared to those predicted using the model. For the predicted ratios, the group weighting factors used to determine S_{Mw} at 37°C were also used to determine S_{Mw} at 25°C.

RESULTS AND DISCUSSION

General Features of the Model

Figure 1 shows a series of curves relating the squared solubility parameter difference, A^2, to the equilibrium solubility for different degrees of polymer cross-linking, as determined from eq. (4), assuming a constant molar volume of 100 cm^3/mol. As expected, there is an inverse relationship between A^2 and S. The rate of change of S for smaller values of A^2 is much greater than that for larger values and the dependence of S on ν is greater for smaller values of A^2. This is consistent with the fact that the restrictive influence of the cross-links will become progressively smaller as the amount of absorbed solvent is reduced (i.e., as A becomes larger). Figure 1 also shows that there is a limit to the maximum solubility that varies inversely with ν. A finite limit for S is expected because cross-linked polymers cannot fully dissolve without breaking covalent bonds. It also follows that larger amounts of solvent can be absorbed at lower cross-link densities.

Figure 2 shows the effect of the solvent molar volume on the predicted solubility for a constant cross-link density of 10^{-4} cm^{-3}. This range of molar volumes includes those of most organic solvents. A constant molecular weight of 100 g/mol was assumed in calculating the solubilities, and the resulting range of densities, from 0.667 to 1.667 g/cm^3, also includes those of most organic solvents. These data show that for an A^2 value of, say, 10 J/cm^3, the predicted solubility will differ by a factor greater than 10 over this range of molar volumes, assuming a constant molecular weight. The influence of molar volume is illustrated in Table II, which lists groups of solvents whose weighted solubility parameter differences (A_w^2, given in Table I and explained below) are very similar but whose molar volumes differ appreciably. In all cases, the solvent with the smaller molar volume has a larger experimental solubility.

Figure 3 shows the predicted variation of S with temperature from 25 to 50°C for three representative solvents: acetone, chloroform, and N-methylpyrrolidone. The linearity of each Arrhenius plot ($r^2 > 0.99$) is consistent with expectations of an exponential dependence of S on temperature.[31,50–52] Although S typically increases with increasing temperature, the opposite behavior has been reported.[23,50] The negative temperature dependence predicted for acetone is confirmed experimentally as shown below. Thus, from this generalized analysis, the model seems to provide results that are consistent with expectations of the effects of cross-linking, molar volume, and temperature.

Model Evaluation for Viton

Table III presents S_E, S_{Mu}, and S_{Mw} for all of the solvents, as well as the ratios of modeled-to-experimental values. Inspection of the S_{Mu} : S_E ratios shows that in relatively few cases do the solubility estimates based on unweighted A^2 values (A_u^2, listed in Table I) provide accurate measures of solubility. The tendency toward underestimation is seen throughout the data and is particularly evident for the aromatic and aliphatic hydrocarbons and the alcohols. At the same time, S_{Mu} values are greater than the corresponding S_E values for the nitro compounds, aldehydes, acetone, and a few of the chlorinated hydrocarbons. The rather poor correlation is better illustrated in the plot of S_{Mu} vs. S_E shown in Figure 4.

One potential source of error in the modeled solubilities is the assumed cross-link density, $\nu = 10^{-4}$

Table I Physical Constants, 3-D Solubility Parameters, and Solvent–Viton® Solubility Parameter Differences

Solvent or Polymer	Mol. Wt. (g/mol)	Density (25°C) (g/cm^3)	Density (37°C) (g/cm^3)	α^a $K^{-1} \times 10^3$
Viton	—	1.86	1.85	0.48
Acetone	58.08	0.784	0.770	1.50
2-Butanone	72.11	0.800	0.788	1.29
4-Methyl-2-pentanone	100.16	0.798	0.785	1.19
3-Pentanone	86.13	0.814	0.798	1.21
Cyclohexanone	98.14	0.944	0.931	1.12
Formamide	45.04	1.127	1.119	0.73
Dimethylformamide	73.09	0.944	0.933	1.03
N-Methylpyrrolidone	99.13	1.026	1.015	0.95
2-Pyrrolidone	85.10	1.120	1.105	0.59
Methanol	32.04	0.787	0.775	1.33
Propanol	60.10	0.804	0.789	1.11
Butanol	74.12	0.810	0.796	1.01
Octanol	130.23	0.821	0.812	0.95
2-Ethoxyethanol	90.12	0.925	0.915	0.95
2-Butoxyethanol	118.17	0.898	0.887	1.04
Carbon disulfide	76.14	1.256	1.238	1.18
Dimethylsulfoxide	78.13	1.101	1.083	1.00
Hexane	86.17	0.655	0.643	1.52
Heptane	100.20	0.679	0.669	1.24
Isooctane	114.23	0.688	0.678	1.20
Benzene	78.11	0.874	0.861	1.21
Toluene	92.14	0.867	0.851	1.09
Xylene	106.17	0.860	0.850	1.01
Ethyl acetate	88.10	0.894	0.875	1.80
2-Ethoxyethylacetate	132.16	0.970	0.962	0.67
Acetonitrile	41.05	0.737	0.721	1.76
Acrylonitrile	53.06	0.800	0.787	1.38
Furfuraldehyde	96.09	1.160	1.142	0.96
Benzaldehyde	106.12	1.044	1.035	0.65
Dioxane	88.11	1.030	1.017	0.94
Tetrahydrofuran	72.11	0.883	0.862	2.02
Nitropropane	89.09	0.982	0.969	1.10
Nitrobenzene	123.11	1.199	1.188	0.78
Methylene chloride	84.93	1.316	1.294	1.46
1,2-Dichloroethane	98.96	1.256	1.229	1.21
Perchloroethylene	165.83	1.623	1.595	1.05
Chloroform	119.38	1.446	1.457	1.53
Methylchloroform	133.41	1.338	1.310	1.26
Trichloroethylene	131.40	1.464	1.435	1.20
Carbon tetrachloride	153.82	1.584	1.561	1.25

cm^{-3}. This is a typical value for lightly cross-linked polymers and, as shown in Figure 1, it also yields reasonable values of solubility as a function of A^2, i.e., the largest predicted values of S at this cross-link density are similar to the largest S_E values shown in Table III.

Decreasing the assumed ν value increases the solubility estimates. However, this does not lead to a significant improvement in the accuracy of modeled S values. Table IV shows the effect on S_{Mu} of changing ν for a few selected solvents. For solvents with relatively large A_u^2 values (i.e., $> 50\ J/cm^3$) and low S_{Mu} values assuming $\nu = 10^{-4}$, decreasing the cross-link density by a factor of two has no measurable

Table I (*continued*)

	Solubility Parameters[b] $(J/cm^3)^{1/2}$			A_u^{2} [c] (J/cm^3)	A_w^{2} [d] (J/cm^3)
	δ_d	δ_p	δ_h		
Viton	17.0	10.3	6.1	—	—
Acetone	15.5	10.4	7.0	3.8	9.5
2-Butanone	16.0	9.0	5.1	4.6	2.0
4-Methyl-2-pentanone	15.3	6.1	4.1	27.7	7.1
3-Pentanone	15.8	7.6	4.7	13.0	3.5
Cyclohexanone	17.8	6.3	5.1	20.0	3.3
Formamide	17.2	26.2	19.0	400.5	156.3
Dimethylformamide	17.4	13.7	11.3	35.0	13.7
N-Methylpyrrolidone	18.0	12.3	7.2	4.6	2.3
2-Pyrrolidone	19.4	17.4	11.3	77.4	33.5
Methanol	15.1	12.3	22.3	256.6	130.5
Propanol	16.0	6.8	17.4	137.6	69.5
Butanol	16.0	5.7	15.8	115.1	58.2
Octanol	17.0	3.3	11.9	85.2	42.6
2-Ethoxyethanol	16.2	9.2	14.3	67.1	28.0
2-Butoxyethanol	16.0	5.1	12.3	68.1	28.7
Carbon disulfide	20.5	0.0	0.6	151.5	83.9
Dimethylsulfoxide	18.4	16.4	10.2	50.4	26.9
Hexane	14.9	0.0	0.0	153.0	34.9
Heptane	15.3	0.0	0.0	151.1	33.0
Isooctane	14.3	0.0	0.0	155.6	37.6
Benzene	18.4	1.0	2.0	109.4	33.8
Toluene	18.0	1.4	2.0	101.2	30.8
Xylene	17.8	0.6	1.4	121.2	36.7
Ethyl acetate	15.8	5.3	7.2	31.7	6.1
2-Ethoxyethylacetate	16.0	4.7	10.6	55.2	8.1
Acetonitrile	15.3	18.0	6.1	56.3	39.0
Acrylonitrile	16.4	17.4	6.8	45.8	30.9
Furfuraldehyde	18.6	14.9	5.1	21.1	34.9
Benzaldehyde	19.4	7.4	5.3	16.3	51.6
Dioxane	19.0	1.8	7.4	82.1	20.7
Tetrahydrofuran	16.8	5.7	8.0	27.9	6.7
Nitropropane	16.2	12.1	4.1	6.9	9.2
Nitrobenzene	20.0	8.6	4.1	16.3	38.0
Methylene chloride	18.2	6.3	6.1	19.6	47.6
1,2-Dichloroethane	19.0	5.3	4.1	35.3	45.1
Perchloroethylene	19.0	6.5	2.9	30.2	40.5
Chloroform	17.8	3.1	5.7	56.6	33.5
Methylchloroform	17.0	4.3	2.0	56.0	33.1
Trichloroethylene	18.0	3.1	5.3	57.4	37.5
Carbon tetrachloride	17.8	0.0	0.6	141.2	39.8

[a] Coefficient of thermal expansion.
[b] Values at 25°C from Ref. 18.
[c] Unweighted 3-D solubility parameter difference determined at 37°C.
[d] Weighted 3-D solubility parameter difference determined at 37°C.

effect on the predicted solubility. For those solvents with smaller A_u^2 values, there is a greater effect. Both of these results are expected in light of Figure 1. For 2-butanone and *N*-methylpyrrolidone, which have very low A_u^2 values, S_{Mu} becomes greater than S_E at the lower cross-link density; however, these are the only solvents for which this occurs. For solvents whose solubilities were initially overestimated, the

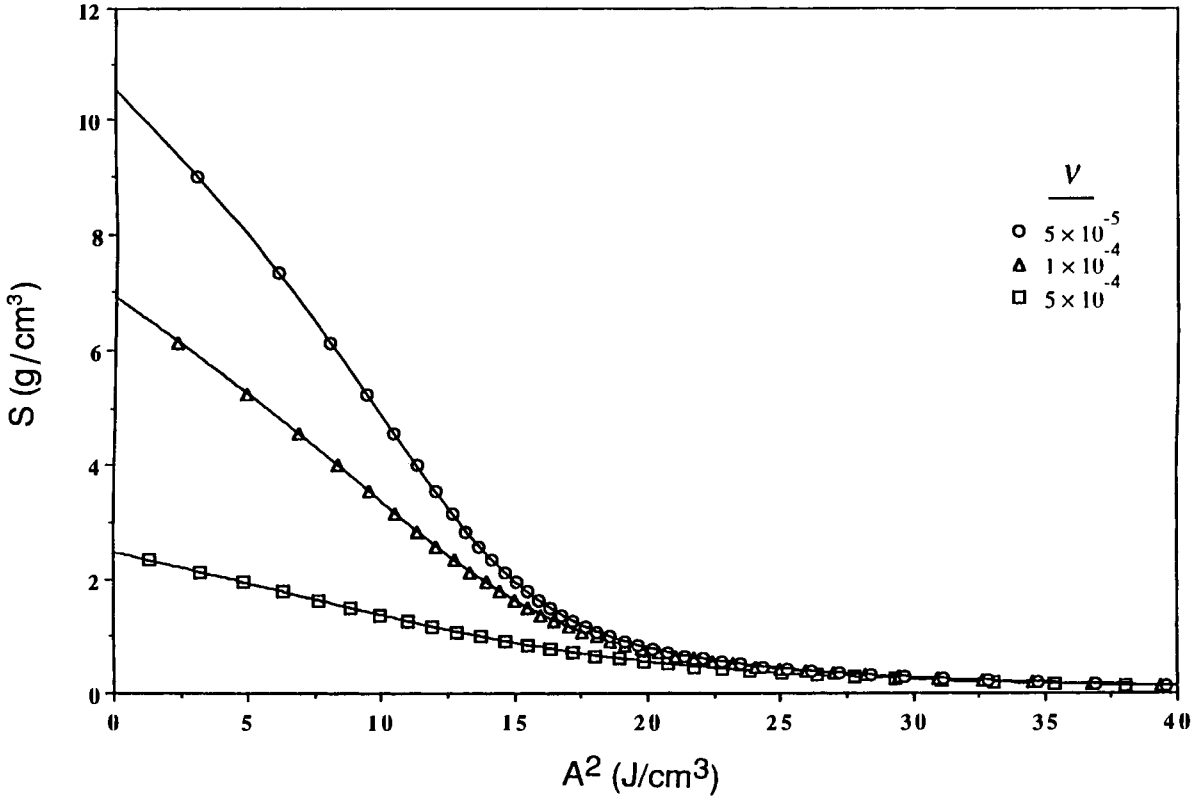

Figure 1 Plot of the squared solubility parameter difference vs. predicted solubility as a function of polymer cross-link density, ν (cm^{-3}). Data were calculated using eq. (4) assuming a constant molar volume of 100 cm^3/mol.

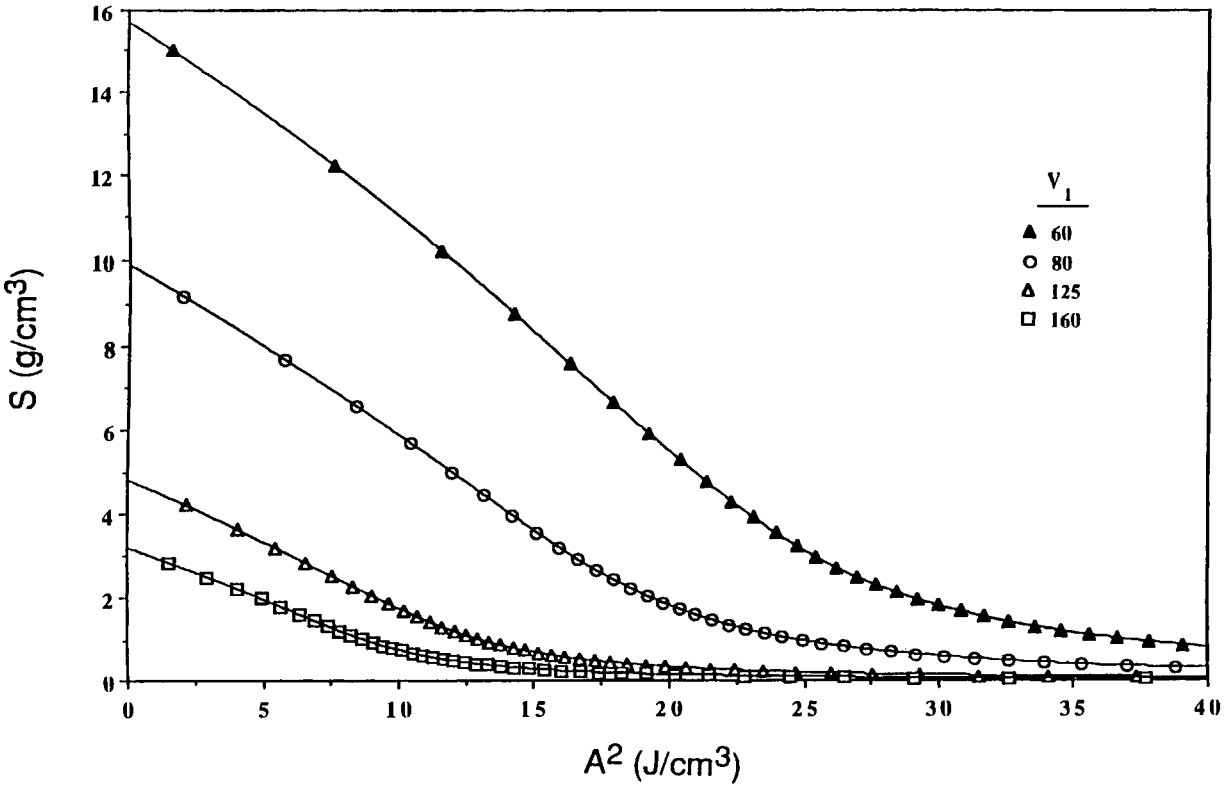

Figure 2 Plot of squared solubility parameter difference vs. predicted solubility as a function of solvent molar volume, V_1 (cm^3/mol). Data were calculated using eq. (4) assuming $\nu = 10^{-4}$ cm^{-3}.

Table II Effect of Solvent Molar Volume on Solubility for Solvent/Viton® Pairs with Similar Weighted Solubility Parameter Differences[a]

Solvent	A_w^2 (J/cm^3)	Molar Volume (cm^3/mol)	S_E (g/cm^3)
Ethyl acetate	6.1	100.7	4.28
Tetrahydrofuran	6.7	83.6	5.15
Nitropropane	9.2	91.9	3.16
Acetone	9.5	75.4	4.22
Toluene	30.8	108.3	0.213
Acrylonitrile	30.9	67.4	0.616
Heptane	33.0	149.7	0.039
Chloroform	33.5	81.9	0.401
2-Pyrrolidone	33.5	77.0	0.875
Nitrobenzene	38.0	103.6	0.213
Trichloroethylene	37.5	89.7	0.316
Carbon tetrachloride	39.8	98.5	0.237
Acetonitrile	39.1	56.9	0.498
Octanol	42.6	160.4	0.030
1,2-Dichloroethane	45.1	80.5	0.228

[a] Data evaluated at 37°C with the exception of tetrahydrofuran and trichloroethylene, which were evaluated at 25°C.

decrease in ν obviously leads to even greater error in S_{Mu}.

If ν is increased by a factor of 5 (i.e., from 10^{-4} to 5×10^{-4}), there is a significant decrease in S_{Mu} for the overestimated solvents, with the magnitude of the effect, again, being greater for solvents with lower values of A_u^2. Although accurate values of S_{Mu} could be obtained for acetone and 2-nitropropane at some intermediate ν value, large errors still remain for the other overestimated solvents as well as for the underestimated solvents (Table IV). Thus, it is clear that the assumed value for the cross-link density by itself cannot account for the observed errors in the modeled values.

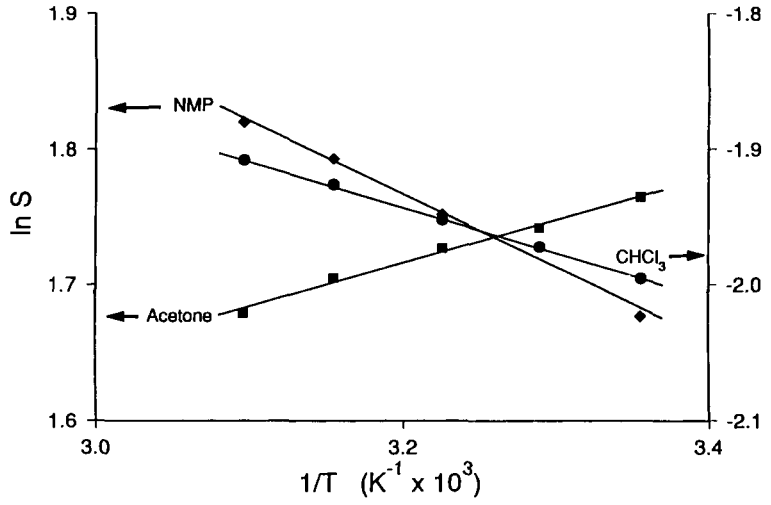

Figure 3 Predicted Arrhenius plots for the representative solvents acetone, *N*-methylpyrrolidone, and chloroform, calculated using eqs. (2), (3) and (7)–(9) and the thermal expansion coefficients listed in Table I.

Table III Experimental and Modeled Equilibrium Solubilities (37°C) Using Unweighted and Weighted Solubility Parameter Differences[a]

Solvent	S_E	S_{Mu}	Ratio S_{Mu}/S_E	Weighting Factor[b]	S_{Mw}	Ratio S_{Mw}/S_E
Ketones						
				a		
Acetone	4.22	5.62	1.33	2.9	4.25	1.01
				b	*a* = 1, *b* = 0.15	
2-Butanone	4.74	4.60	0.97	0.86	5.40	1.14
4-Methyl-2-pentanone	3.94	0.154	0.03	0.003	2.70	0.69
3-Pentanone	4.14	1.65	0.40	0.25	4.44	1.07
Cyclohexanone	3.67	0.685	0.19	0.41	5.34	1.45
Amides						
				b	*a* = 1, *b* = 0.39	
Formamide	0.026	0.0008	0.03	0.47	0.047	1.82
Dimethylformamide	3.57	0.350	0.10	0.38	3.50	0.98
N-Methylpyrrolidone	6.18	5.75	0.93	0.67	6.54	1.06
2-Pyrrolidone	0.875	0.054	0.06	0.30	0.48	0.55
Alcohols						
				b	*a* = 1, *b* = 0.50	
Methanol	0.110	0.005	0.04	0.37	0.055	0.50
Propanol	0.031	0.005	0.17	0.60	0.055	1.74
Butanol	0.024	0.005	0.20	0.65	0.051	2.14
Octanol	0.030	0.002	0.05	0.48	0.026	0.88
Glycol ethers						
				b	*a* = 1, *b* = 0.41	
2-Ethoxyethanol	0.394	0.033	0.08	0.38	0.337	0.86
2-Butoxyethanol	0.117	0.011	0.09	0.45	0.143	1.23
Sulfur compounds						
				b	*a* = 1, *b* = 0.52	
Carbon disulfide	0.117	0.013	0.12	0.47	0.092	0.84
Dimethyl sulfoxide	0.855	0.201	0.24	0.56	1.03	1.20
Aliphatic hydrocarbons						
				b	*a* = 1, *b* = 0.20	
Hexane	0.056	0.00008	0.002	0.21	0.062	1.11
Heptane	0.039	0.00004	0.001	0.23	0.055	1.42
Isooctane	0.035	0.000009	0.0003	0.18	0.028	0.78
Aromatic hydrocarbons						
				b	*a* = 1, *b* = 0.30	
Benzene	0.154	0.007	0.05	0.36	0.243	1.59
Toluene	0.213	0.005	0.02	0.29	0.194	0.91
Xylene	0.137	0.0009	0.006	0.25	0.086	0.63
Esters						
				b	*a* = 1, *b* = 0.13	
Ethyl acetate	4.28	0.224	0.05	0.14	4.38	1.02
2-Ethoxyethyl acetate	2.69	0.022	0.008	0.12	2.57	0.95
Nitriles						
				b	*a* = 1, *b* = 0.67	
Acetonitrile	0.498	0.185	0.35	0.66	0.481	0.97
Acrylonitrile	0.616	0.221	0.36	0.67	0.622	1.01

Table III *(Continued)*

Solvent	S_E	S_{Mu}	Ratio S_{Mu}/S_E	Weighting Factor[b]	S_{Mw}	Ratio S_{Mw}/S_E
Aldehydes						
				a	*a* = 8.0, *b* = 1	
Furfuraldehyde	0.393	1.38	3.51	8.3	0.362	0.92
Benzaldehyde	0.065	1.42	21.9	7.8	0.071	1.10
Ethers						
				b	*a* = 1, *b* = 0.22	
Dioxane	1.28	0.023	0.02	0.21	1.20	0.94
Tetrahydrofuran[c]	5.15	0.494	0.10	0.22	5.21	1.01
Nitro compounds						
				a	*a* = 3.6, *b* = 1	
Nitromethane	0.167	0.189	1.14	3.1	0.162	0.97
Nitropropane	3.54	5.03	1.42	5.8	4.36	1.38
Nitrobenzene	0.213	1.59	7.46	3.3	0.226	0.72
Chlorinated hydrocarbons						
				b	*a* = 1, *b* = 2.5	
Methylene chloride	0.352	3.93	11.2	2.5	0.352	1.00
				a	*a* = 4.1, *b* = 1	
1,2-Dichloroethane	0.228	0.424	1.86	4.1	0.228	1.00
Perchloroethylene[c]	0.159	0.376	2.36	4.1	0.160	1.01
				b	*a* = 1, *b* = 0.59	
Chloroform	0.401	0.143	0.36	0.66	0.549	1.36
Methylchloroform	0.386	0.073	0.19	0.53	0.292	0.76
Trichloroethylene[c]	0.316	0.094	0.30	0.62	0.359	1.14
				b	*a* = 1, *b* = 0.28	
Carbon tetrachloride	0.237	0.003	0.01	0.28	0.238	1.00

[a] S_E = experimental solubility values. S_{Mu} = modeled solubility values calculated without weighting factors. S_{Mw} = modeled solubility values calculated using the group weighting factors (*a*,*b*) shown above the S_{Mw} values. Units of solubility are g/cm^3.
[b] Values of weighting factors required for $S_{Mw} = S_E$ for each solvent.
[c] Based on data collected at 25°C.

Another important assumption made in the model is that $\chi_S = 0$. For the range of ν examined, this assumption is consistent with most of the data since any value of χ_S would lead to even lower modeled solubility values than those shown in Tables III and IV (recall that $\chi_S > 0$). For the overestimated solvents, it is possible that the assumption of $\chi_S = 0$ is not valid.

To examine this issue, experimental volume fractions were used in eq. (2) to solve for χ and then the χ_S values for the overestimated solvents were determined by difference from eq. (3). The resulting values, listed in Table V, range from 0.17, for acetone, to 1.48, for benzaldehyde. Although this approach succeeds in reconciling modeled and experimental solubility values, the χ_S values show no systemmatic pattern, i.e., solvents containing the same functional groups, which might be expected to have similar specific interactions with the Viton®, have widely different χ_S values. Coupled with the fact that there is no way to correct for the underestimated cases using χ_S, it does not appear feasible to rely on χ_S as a correction factor for use in a generalized model.

The factor thought to be primarily responsible for the observed error in the S_{Mu} values is inaccuracy in the 3-D solubility parameter differences. As discussed above, there is evidence showing that a single set of 3-D solubility parameters cannot account for the varying influences of inductive or other forces

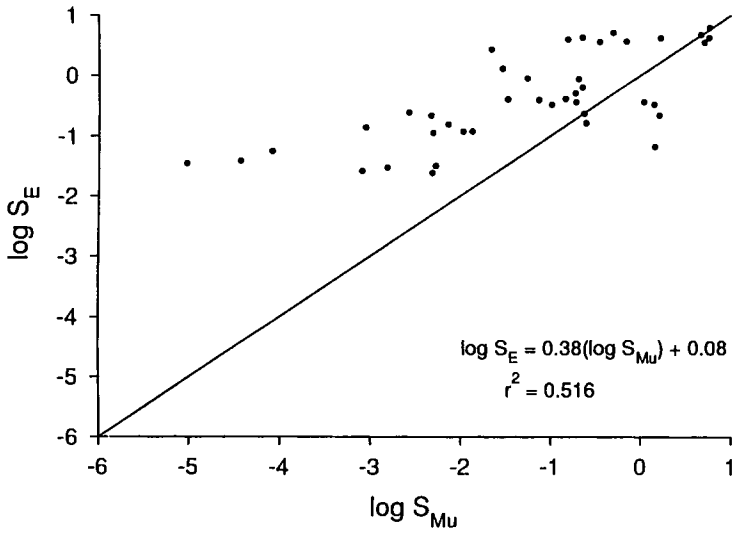

Figure 4 Log–log plot of unweighted modeled solubilities (S_{Mu}) vs. experimental solubilities (S_E) for 40 solvents in Viton® (r^2 obtained from linear regression). Solid line represents perfect correlation.

in the overall solubility interaction between different solvents and polymers and that weighting factors are needed to account for this.

Values of a and b were therefore calculated for each of the solvents. First, experimental volume fractions were used in eq. (4) to solve for A. Then, using temperature-corrected solubility parameter values in eq. (6), a or b (see below) was varied iteratively until the modeled and experimentally derived A values were in agreement. The resulting solvent-specific values of a and b are listed in Table III. In an attempt to rectify the errors in modeled solubilities while retaining some generality in the model, solvents were organized according to chemical class and values of a and b were calculated for each class, where possible, that minimized the error in the modeled values for the class as a whole.

Cases in which $S_{Mu} < S_E$ were considered to result from the large differences between the dipole–dipole and hydrogen-bonding solubility parameters of the solvent and Viton®, and these were subsequently weighted to reduce their influence on the total sol-

Table IV Effect of Assumed Cross-link Density, ν, on Unweighted Predicted Solubilities of Selected Solvents[a]

		S_{Mu}/S_E		
Solvent	A_u^2	$\nu = 5 \times 10^{-5}$	$\nu = 1 \times 10^{-4}$	$\nu = 5 \times 10^{-4}$
Methanol	256.6	0.04	0.04	0.04
Hexane	153.0	0.001	0.001	0.001
Benzene	109.4	0.05	0.05	0.05
Acetonitrile	56.3	0.37	0.37	0.35
Chloroform	56.6	0.36	0.36	0.34
3-Pentanone	13.0	0.79	0.40	0.19
N-Methylpyrrolidone	4.6	1.41	0.93	0.34
2-Butanone	4.6	1.47	0.97	0.36
Furfuraldehyde	21.1	4.80	4.33	2.84
Benzaldehyde	16.3	25.2	21.9	12.9
Nitropropane	6.9	2.41	1.58	0.60
Acetone	3.8	2.03	1.33	0.49

[a] Units of ν are cm^{-3}.

Table V χ, χ_H, and χ_S for Solvents with $S_{Mu} > S_E$[a]

Solvent	χ	χ_H	χ_S
Acetone	0.28	0.11	0.17
Furfuraldehyde	1.20	0.69	0.51
Benzaldehyde	2.12	0.65	1.47
Nitropropane	0.43	0.25	0.18
Nitrobenzene	1.42	0.65	0.77
Methylene chloride	1.21	0.50	0.71
1,2-Dichloroethane	1.41	1.10	0.31
Perchloroethylene	1.79	1.22	0.57

[a] χ was determined from experimental volume fractions using eq. (2), χ_H was determined using unweighted solubility parameter differences, and χ_S was determined from $\chi - \chi_H$.

ubility parameter difference. For the cases in which $S_{Mu} > S_E$, there was a choice of whether to increase either a or b or both factors. For all such solvents, it was sufficient to adjust only one of the weighting factors. The choice of whether to increase a or b was arbitrary, with the exception of methylene chloride: The dispersion parameters for methylene chloride and Viton® are similar enough that even large values of a had little effect on the modeled solubility and increasing b was the only way to rectify the modeled and experimental values.

In attempting to calculate group weighting factors, however, it was found that significantly better agreement between modeled and experimental solubilities for the members of a given class was obtained by increasing a rather than b (methylene chloride remained the exception). The need for weighting factors greater than unity to adjust the modeled solubilities has not been previously reported, and beyond their representation of some property that reduces the expected solvent–polymer interaction strength, their physical interpretation is not yet clear.

The calculated group weighting factors are presented in Table III and the resulting A_w^2 values, based on the weighting factors determined for each group, are listed in the last column of Table I (note: individual weighting factors were used to determine A_w^2 for acetone, methylene chloride, and carbon tetrachloride). In most cases, a single weighting factor was sufficient to bring the predicted solubilities for all solvents in a class within a factor of about two of experimental values, but there were exceptions. The chlorinated hydrocarbons, for example, required four different weighting factors to obtain satisfactory results. However, it is well known that the dispersion parameters of chlorinated hydrocarbons are rather imprecise.[15,37] Any error in δ_d will also create error in the assigned value of δ_h because it is determined on the basis of δ_d. In addition, inclusion of all chlorinated solvents in a single class has only a tenuous basis in terms of solubility: The nonpolar carbon tetrachloride would not be expected to have solubility properties similar to those of the more polar unsymmetrically substituted chlorinated solvents or those containing double-bonded carbon atoms. Thus, it is not unexpected to see such disparities between assigned weighting factors for the chlorinated solvents.

With respect to the ketones, acetone is the only solvent that is overestimated using A_u^2. As shown in Table I, however, acetone has the lowest value of A_u^2 and is, therefore, the most sensitive to the assumed value of ν. If ν is increased by only a small amount (i.e., from 1×10^{-4} to 1.55×10^{-4} cm^{-3}), the S_{Mu} value for acetone becomes less than S_E. Of course, this change of ν also affects S_{Mu} for the other solvents, but as the data presented in Table IV suggest, the change in S_{Mu} is negligibly small for most solvents. Even for the other solvents with relatively low A_u^2 values, the order of S_{Mu} and S_E does not change (i.e., solubilities overestimated assuming $\nu = 10^{-4}$ cm^{-3} are still overestimated for $\nu = 1.55 \times 10^{-4}$ cm^{-3}). The individual weighting factors for these solvents do change slightly, but the group weighting factors remain unaffected in all cases. Although speculative (since ν is not known), this does provide a tenable explanation for the apparently anomalous modeled behavior of acetone.

It is recognized that many of the other classes of solvents are represented by only two or three members and that the group weighting factors established here may not be applicable to untested members. Yet for most classes, aside from the principal functional group used to define the class, the solvents examined do incorporate a diversity of structural features. Having stated this, it must also be acknowledged that grouping carbon disulfide and dimethylsulfoxide together and applying a common weighting factor to these solvents is viewed with some skepticism: It may be fortuitous that they can be represented accurately by a single weighting factor since they clearly have very different solvent properties.

The S_{Mw} values shown in Table III are in all cases within a factor of 2.2 of the corresponding S_E values. The amides and alcohols show the greatest within-

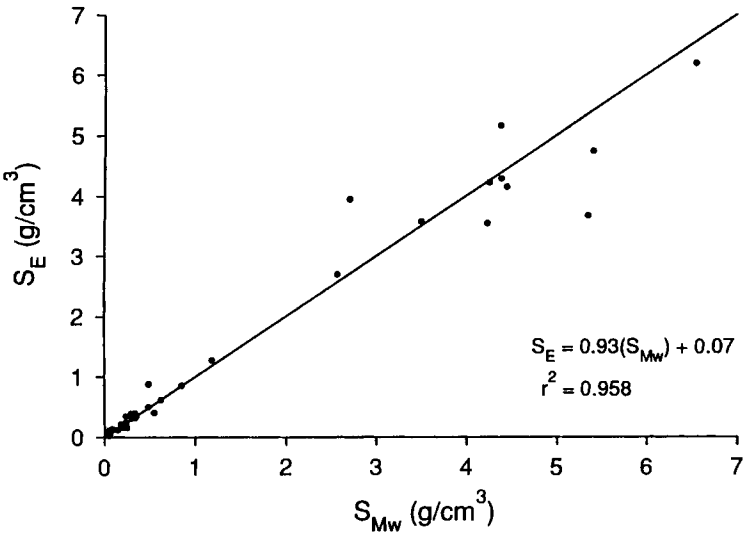

Figure 5 Plot of weighted modeled solubilities (S_{Mu}) vs. experimental solubilities (S_E) for 40 solvents in Viton® (r^2 obtained from linear regression). Solid line represents perfect correlation.

class range in the modeled-to-experimental ratios, which is not too surprising given the range of structures represented. Given that the S_{Mu} : S_E ratios differ widely between the members in many of the individual classes, it is remarkable that a single set of weighting factors can bring all of the modeled values into such close agreement with the experimental values: See, for example, the aldehydes, nitro compounds, and amides. This supports the notion that the weighting factors are not merely arbitrary correction factors, but rather that they are reflecting some relevant physical or chemical properties of the solvents. Figure 5 shows the expected strength of the correlation between S_{Mw} and S_E for all of the solvents.

In Table VI, the weighting factors determined in this study are compared to those reported by Ashton et al.[46] for the solvents common to both studies. In the latter study, *b* factors were calculated using the Hildebrand–Scratchard equation and were based on the infinite-dilution activity coefficient of one solvent dissolved in another. The Flory–Rehner equation used here, which is applicable to solvent–polymer systems, is analogous to the Hildebrand–Scratchard equation.

Since the solvent mixtures used in the previous study were not specified, it is not possible to make a detailed comparison. At the outset, some differences in weighting factors would be expected because of the use of a cross-linked polymer and finite (often high) solvent concentrations in this study as opposed to the use of solvent–solvent mixtures and a focus on the very dilute concentration range in the

Table VI Comparison of Weighting Factors Determined in this Study with Those Reported by Ashton et al.[46]

Solvent	Ashton *b*	This Study[a] *a*	This Study[a] *b*
Hexane	0.22		0.21 (0.20)
Heptane	0.20		0.23 (0.20)
Isooctane	0.17		0.18 (0.20)
Benzene	0.15		0.36 (0.30)
Toluene	0.064		0.29 (0.30)
Ethylbenzene	0.12		—
Xylene	—		0.25 (0.30)
Chloroform	0.22		0.67 (0.59)
Carbon tetrachloride	0.24		0.28 (0.59)
Trichloroethylene	0.20		0.62 (0.59)
Perchloroethylene	0.24	4.1 (4.1)	
Acetone	0.14	2.9	— (0.15)
2-Butanone	0.14		0.86 (0.15)
4-Methyl-2-pentanone	0.13		0.003 (0.15)
Ethyl acetate	0.14		0.14 (0.13)
Methanol	0.26		0.37 (0.50)
1-Propanol	0.24		0.60 (0.50)
1-Butanol	0.24		0.65 (0.50)
Octanol	0.23		0.48 (0.50)
Dioxane	0.10		0.21 (0.22)
Furfural	0.26	8.3 (8.0)	

[a] Values in parentheses are group values determined in this study.

previous study. Nevertheless, a few trends can be identified.

The agreement in b values is quite good for the aliphatic hydrocarbons and for carbon tetrachloride, which might be attributed to the low polarity and polarizability of these solvents. Surprisingly, the b values for ethyl acetate are the same and the ketone values determined in the previous study are very close to the group value determined here. For the remaining solvents, the b values from this study are generally higher and more variable between classes, which is most likely due to the use of the highly polar Viton® as the other mixture component.

Self-association (see below) may be responsible for the low methanol value observed here relative to the other alcohols, which was not found by Ashton et al. Divergence in the b values within a given group, found here for the ketones, is also seen in their data for the aromatic solvents (i.e., for toluene). As stated above, the weighting factor required for acetone in this study may be an artifact of the assumed cross-link density. The most striking difference is the need for b values ≥ 1 and a values > 1 in this study. Nonetheless, the similarities in the values and/or trends in the weighting factors between the two studies lend credence to their physical or chemical significance and their applicability in modeling solubility.

Temperature Effects

Table VII presents data comparing the experimental and predicted effects of temperature on solubility between 25 and 37°C for 17 solvents. In most cases, the change in the experimental solubility was small over this range of temperatures, consistent with previous reports.[31,50,51] The fact that permeation rates are often strongly affected by temperature is thought to be due to the effects of temperature on the diffusion coefficient rather than on equilibrium solubility.[51] Notably, the model correctly predicts the decrease in solubility with increasing temperature observed for all the ketones, ethyl acetate, and 2-nitropropane. Overall, the ability of the model to account for temperature was quite good: Errors in predicted vs. experimental ratios ranged from 1 to 19%, giving an average absolute error of 6% of the experimental ratio values.

Both methanol and 2-ethoxyethanol were incorrectly predicted to increase in solubility with increasing temperature. These errors can be ascribed to the unique propensity for intermolecular cluster formation with these solvents. Myers and Abu-Isa[23] showed for methanol, in contrast to other alcohols, that the stability of the clusters are very sensitive to temperature and that disruption of the cluster

Table VII Comparison of Experimental and Modeled Temperature Effects[a]

Solvent	Solubility Ratio ($S_{37°C}/S_{25°C}$)			
	Experimental	Modeled	Error	% Error[b]
Acetone	0.93	0.89	−0.04	−4
2-Butanone	0.96	0.98	+0.02	+2
4-Methyl-2-pentanone	0.93	0.95	+0.02	+2
3-Pentanone	0.93	0.97	+0.04	+4
N-Methylpyrrolidone	1.05	1.03	−0.02	−2
1-Propanol	1.35	1.20	−0.15	−11
Carbon disulfide	1.22	1.15	−0.07	−6
Acetonitrile	1.04	1.07	+0.03	+3
Toluene	1.06	1.10	+0.04	+4
Ethyl acetate	0.89	0.94	+0.05	+6
Dioxane	1.01	1.17	+0.16	+16
Nitropropane	0.99	0.98	−0.01	−1
Nitrobenzene	1.05	1.25	+0.20	+19
Methylene chloride	1.03	1.04	+0.01	+1
Methylchloroform	1.10	1.28	+0.18	+16
Mean absolute % error				6
Methanol	0.80	1.18	—	—
2-Ethoxyethanol	0.73	1.16	—	—

[a] Modeled solubility values at both temperatures were determined using the group weighting factors listed in Table III.
[b] Calculated using experimental ratio as the expected value.

causes the decrease in Viton® solubility with temperature. A similar phenomenon probably occurs with 2-ethoxyethanol.

Comparison with Conventional Use of Solubility Parameters

Finally, it is useful to compare the results obtained with the current modeling approach to those obtained using the more common approach reported for correlating solubility parameters with solvent–CPC permeation indices (i.e., S, BT, and SSPR). As discussed above, the conventional approach has been to use weighting factors of $a = 4$ and $b = 1$ in eq. (6) for calculating A and then to use A as a relative index of solubility or permeation for various solvents vs. a given CPC polymer. Figure 6 presents a plot of A determined in this way, referred to as A_{a4} vs. S_E for the solvents examined in this study. Although the expected inverse relationship is apparent, the correlation between A_{a4} and S_E is quite poor: For low-to-moderate values of A_{a4}, a wide range of solubilities is found for similar A_{a4} values, and for large values of A_{a4}, very similar solubilities are found for quite different values of A_{a4}. The trend in the data shown in Figure 6 suggests a logarithmic relationship between these variables; however, a plot of A_{a4} vs. ln S_E yielded a linear regression r^2 value of only 0.55. Results reported by Perkins et al.[12] show similar correlations between A_{a4} and both ln BT and ln SSPR for solvents in Viton®. It is apparent, for this set of solvent–polymer mixtures at any rate, that the conventional approach does not provide a very accurate means of estimating solubility or permeation resistance.

CONCLUDING REMARKS

An approach for using 3-D solubility parameters to model equilibrium solvent–CPC solubilities has been presented and evaluated. The model permits independent examination of the influence of several key variables not previously incorporated into solubility parameter-based permeation models, including the CPC–polymer cross-link density, solvent molar volume, and exposure temperature. The predicted effect of temperature on solubility was within 6%, on average, of that found experimentally. Temperature effects were incorrectly predicted for methanol and 2-ethoxyethanol owing, apparently, to self-association via hydrogen-bonding with these solvents.

Limitations attributed principally to the inability of a single set of 3-D solubility parameters to account for variations in solubility interactions as function of the solvent and polymer necessitate the use of empirically determined weighting factors to obtain accurate solubility estimates. Although this limits the predictive capacity of the model, the weighting factors appear to be related to the structures of the solvents: For the solvent/Viton® combinations examined here, grouping by chemical class results in reasonably accurate solubility estimates (within a factor of two of experimental values) with a single set of weighting factors in most cases. Many of the weighting factors determined in this study are com-

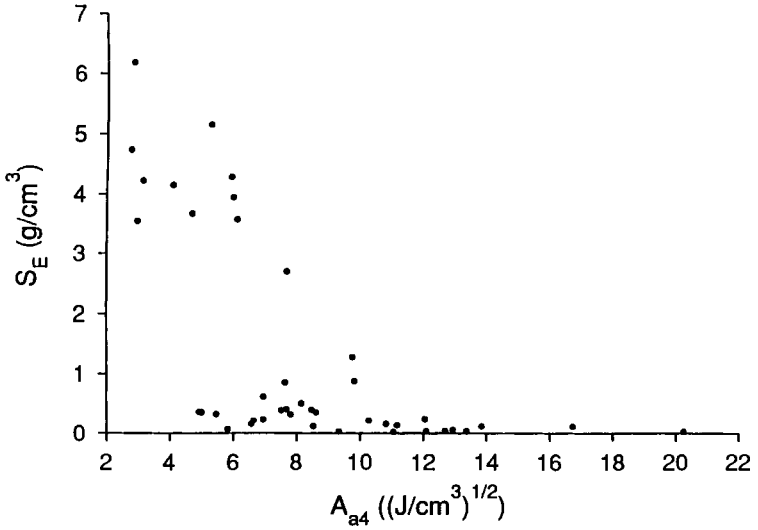

Figure 6 Plot of A_{a4} vs. S_E, where A_{a4} is the absolute value of the solubility parameter difference calculated from eq. (6) using weighting factors of $a = 4$ and $b = 1$.

parable to those determined in previous studies of solvent–solvent solubilities, adding further support to their use as indicators of physical or chemical properties affecting solubility. Additional studies are needed to determine whether the weighting factors can be correlated with other properties that would allow their prediction, *a priori,* and to determine the applicability of this modeling approach to other solvent–CPC systems. Efforts toward these goals are currently underway.

The conventional practice of multiplying the dispersion solubility parameter term by four when calculating solvent–polymer solubility parameter differences was shown to yield large errors in estimated solubilities for the solvents examined here. Based on these results, it is recommended that this approach to ranking solvents with respect to relative solubility or permeability be reconsidered.

From a practical standpoint, the need for the CPC–polymer cross-link density in the model is problematic because this information is not readily available for most CPC–polymers. Although it was shown that for moderately soluble or poorly soluble solvents the cross-link density has little effect on predicted solubility values, for the more soluble solvents, it is more critical. CPC manufacturers might be encouraged to make such data available.

Separate estimates of the solvent diffusion coefficients are needed in order to estimate BT and SSPR with this approach. As shown in the article that follows, diffusion coefficients can be modeled quite accurately using correlations in which A_w or χ, based on weighted 3-D solubility parameter differences, are predictor variables. Modeled values of S and D are then used in Fickian diffusion models to estimate BT and SSPR values for a subset of the solvents examined here.

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