Solubility Parameter Values

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A. INTRODUCTION

Applications of solubility parameters include selecting compatible solvents for coating resins, predicting the swelling of cured elastomers by solvents, estimating solvent vapor pressure in polymer solutions for devolatilization and reaction systems (16), and predicting phase equilibria for polymer–polymer (107), polymer–binary (93), random copolymer (102), and multicomponent solvents (38, 98,108,109).

Cohesive energy density and solubility parameters are defined in the section on miscibility of solvents and polymers (Section B). In addition, the applicability of solubility parameters to thermodynamic calculations and their limitations are discussed. Section C contains methods for measuring, calculating and correlating solubility parameters of solvents and polymers. Section D contains

alphabetical listings of solubility parameters (Table 7), a list of solubility parameters in rank order (Table 8), a list of three-component solubility parameters of solvents (Table 9), and a list of solubility parameters of polymers (Table 10). With the exception of Table 7, solubility parameter values are reported in $MPa^{1/2}$ units. The table showing solubility parameter value ranges for polymers (Table 3.4 in the third edition) has not been reproduced here.

B. MISCIBILITY OF SOLVENTS AND POLYMERS

1. Cohesive Energy Density and the Solubility (Hildebrand) Parameter

Dissolution of an amorphous polymer in a solvent is governed by the free energy of mixing

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{B1}$$

where ΔG_m is the Gibbs free energy change on mixing, ΔH_m is the enthalpy change on mixing, T the absolute temperature, and ΔS_m is the entropy change on mixing. A negative value of the free energy change on mixing means that the mixing process will occur spontaneously. Otherwise, two or more phases result from the mixing process. Since the dissolution of a high molecular weight polymer is always connected with a small or modest increase in entropy, the enthalpy term (the sign and magnitude of ΔH_m) is the deciding factor in determining the sign of the Gibbs free energy change. Solubility parameters were developed to describe the enthalpy of mixing of simple liquids (nonpolar, nonassociating solvents), but have been extended to polar solvents and polymers.

Hildebrand and Scott (59) and Scatchard (101) proposed that

$$\Delta H_m = V\left(\left(\frac{\Delta E_1^v}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2^v}{V_2}\right)^{1/2}\right)^2 \phi_1\phi_2 \tag{B2}$$

where V is the volume of the mixture, ΔE_i^v the energy of vaporization of species i, V_i the molar volume of species i, and ϕ_i the volume fraction of i in the mixture. ΔE_i^v is the energy change upon isothermal vaporization of the saturated liquid to the ideal gas state at infinite volume (94). The cohesive energy density (CED), ΔE_i^v, is the energy of vaporization per cm^3. The solubility parameter has been defined as the square root of the cohesive energy density and describes the attractive strength between molecules of the material.

$$\delta_i = \left(\frac{\Delta E_i^v}{V_i}\right)^{1/2} \tag{B3}$$

The dimensions of δ_i are

$$(cal/cm^3)^{1/2} = (4.187\,J/10^{-6}\,m^3)^{1/2} = 2.046 \times 10^3 (J/m^3)^{1/2} = 2.046\,MPa^{1/2} \tag{B4}$$

The solubility parameter can be interpreted as the "internal pressure" of the solvent (9–11). δ_i is called the Hildebrand parameter by some authors. Other researchers (13) prefer the term, "cohesion parameter", since it correlates with a large number of physical and chemical properties, and not just the miscibility of the components. The solubility parameter of a mixture is often taken as the sum of the products of the component solubility parameters with their volume fractions:

$$\delta_{mixture} = \sum_i \delta_i\phi_i \tag{B5}$$

Relation between δ_1 and ΔH_m Equation (B2) can be rewritten to give the heat of mixing per unit volume for a binary mixture:

$$\frac{\Delta H_m}{V} = (\delta_1 - \delta_2)^2\phi_1\phi_2 \tag{B6}$$

Equation (B6) gives the heat of mixing of regular solutions in which the components mix with: (a) no volume change on mixing at constant pressure, (b) no reaction between the components, and (c) no complex formation or special associations (114). The heat of mixing must be smaller than the entropic term in Eq. (B1) for polymer–solvent miscibility ($\Delta G_m \leq 0$). When $\delta_1 = \delta_2$, the free energy of mixing will always be less than zero for regular solutions and the components will be miscible in all proportions. In general, the solubility parameter difference, $(\delta_1 - \delta_2)$ must be small for miscibility over the entire volume fraction range.

Relation between δ_1 and ΔH_1^v The energy change on isothermal vaporization can be related to the enthalpy of vaporization:

$$\Delta E_i^v = \Delta H_i^v + \Delta H_i^\infty - RT + p_i^s V_i \tag{B7}$$

where ΔH_i^v is the enthalpy of vaporization at standard conditions, ΔH_i^∞ the molar increase in enthalpy on isothermally expanding the saturated vapor to zero pressure, R the ideal gas constant, and p^s the saturation vapor pressure at temperature, T. At pressures below 1 atm, the ΔH_i^∞ and $p^s V_i$ terms are usually much less than the ΔH_i^v and RT terms, and Eq. (B7) reduces to Eq. (B8):

$$\Delta E_i^v = \Delta H_i^v - RT \tag{B8}$$

The solubility parameter of volatile materials (solvents for example) can be determined by measuring their enthalpy of vaporization or using a correlation for this quantity, and using Eq. (B9):

$$\delta_i = \left(\frac{\Delta H_i^v - RT}{V_i}\right)^{1/2} \tag{B9}$$

Equation (B9) should be used at pressures near 1 atm. Near the critical point, $\Delta H_i^v = 0$, and Eq. (B8) incorrectly

predicts a negative value for the cohesive energy density while Eq. (B7) yields a small positive value.

Dissolution of crystalline polymers The free energy of mixing for crystalline polymers contains terms for the free energy of fusion for the crystalline volume fraction of the material. The free energy of fusion may contain terms that account for the loss of crystallite surface area and the mixing of amorphous material with oriented material. These terms would be added to Eq. (B1). The enthalpy of mixing could still be modeled using Eqs. (B2) or (B6). Some crystalline polymers obey the solubility parameter model at temperatures near their melting point, $T > 0.9T_m$ (123). Solvent swelling experiments with crystalline polymers may fit Eq. (B1), particularly if the solvent is a poor one for the polymer and does not significantly dissolve crystalline regions.

2. Cohesive Energy Parameters for Polar Systems

The solubility parameter describes well the enthalpy change on mixing of nonpolar solvents but does not always give reliable results when extended to polar systems. The free energy change of mixing for polar systems is dominated by hydrogen-bonding forces between various groups in the solvent and polymer. Hydrogen-bonding forces are much stronger than van der Waals or dipole forces and often dominate the free energy of mixing. Complete miscibility is expected to occur if the solubility parameters are similar and the degree of hydrogen bonding (p: poor, m: moderate and s: strong) is similar between the components. Hydrocarbons, chlorinated hydrocarbons and nitrohydrocarbons are considered to be poor hydrogen-bonding solvents. Ketones, esters, and glycol monoethers give moderate hydrogen bonding. Alcohols, amines, acids, amides and aldehydes are strong hydrogen-bonding solvents. Table 7 classifies materials using these categories (21–24). Alternative classifications have been given by Lieberman (69), Gardon (41,85,86) and Dyck and Hoyer (32).

Other investigators have decomposed the Hildebrand parameter into several terms representing different contributions to the free energy of mixing. Hildebrand (59) used dispersive and polar solubility terms for solvents, with the complete parameter being given by

$$\delta^2 = \delta_d^2 + \delta_p^2 \tag{B10}$$

where δ_d is the dispersive term and δ_p the polar term. The additional term improved agreement between δ and experimental data. Prausnitz and coworkers accounted for polar bonding by including parameters for permanent dipole interactions and dispersion type interactions. This approach has been applied to polymer solutions (15) and complex formation (57). Crowley et al. (26,27) proposed a three-parameter system.

Hansen (49–53,56) and Hansen and Skaarup (54) assume that the cohesive energy arises from dispersive, permanent dipole–dipole interactions and hydrogen bonding forces:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{B11}$$

where δ_h accounts for a variety of association bonds, including hydrogen bonds and permanent dipole-induced dipole (47). The values of these components for solvents were calculated from a large number of solubility data sets. Polymer solubility parameters can also be decomposed to a three-term set. The Hansen parameters give improved agreement with data but are still not completely accurate in predicting solutions thermodynamics for every system. Peiffer (172) has related dispersion, polar and induced solubility parameters to intermolecular forces and molecular size. The dispersive component increases with molecular size, while the polar component decreases with molecular size.

Temperature effects The solubility parameter decreases with temperature. The individual terms have varied dependence on temperature, namely (Ref. 55)

$$\begin{aligned} \frac{d\delta_d}{dT} &= -1.25 \times \alpha \times \delta_d \\ \frac{d\delta_p}{dT} &= -\frac{\delta_p \times \alpha}{2} \\ \frac{d\delta_p}{dT} &= -\delta_h\left(1.22 \times 10^{-3} + \frac{\alpha}{2}\right) \end{aligned} \tag{B12}$$

where $\alpha(K^{-1})$ is the volumetric thermal expansion coefficient.

3. Relationship between Solubility Parameters and other Thermodynamic Parameters

Hildebrand and Hansen parameters can be calculated using other thermodynamic quantities. This section contains some of the relationships for binary systems. Extensions to multicomponent systems are described by Flory (37) and Olabisi et al. (89).

Activity coefficients Excess free energy calculations for regular solutions (93) can be used to relate solubility parameters and solvent activity coefficients:

$$RT \ln\gamma_1 = V_1\phi_2^2(\delta_1 - \delta_2)^2 \tag{B13}$$

$$RT \ln\gamma_2 = V_2\phi_1^2(\delta_1 - \delta_2)^2 \tag{B14}$$

where γ_i is the activity coefficient of component i. Equations (B13) and (B14) depend on the use of the geometric mean, $\delta_{12} = (\delta_1 \times \delta_2)^{1/2}$. Funk and Prausnitz (40) show that there are deviations from this rule for aromatic hydrocarbons.

Molar excess free energy of mixing The molar excess free energy of mixing for binary solutions is

$$\Delta G^E = \sum_i (\delta_{1-i} - \delta_{2-i})^2 \tag{B15}$$

where δ_{j-i} is the solubility term of group i for species j.

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Polymer–solvent interaction parameter The polymer–solvent interaction parameter, χ, is modeled as the sum of entropic and enthalpic components:

$$\chi = \chi_H + \chi_S \tag{B16}$$

where χ_H is the enthalpic component and χ_S is the entropic component. χ_S is usually taken to be a constant between 0.3 and 0.4 for nonpolar systems: $\chi_S = 0.34$ is often used (15,104). The enthalpic component can be related to the Hildebrand parameters:

$$\chi_H = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \tag{B17}$$

Substituting Eq. (B17) into Eq. (B16)

$$\chi = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 + 0.34 \tag{B18}$$

Equation (B18) permits only positive values of the interaction parameter. Since the Flory–Huggins criterion for complete solvent–polymer miscibility is $\chi < 0.5$, the enthalpic contribution must be small and the solubility parameters of the solvent and polymer must be similar (21). The molar volume of the solvent also affects miscibility and phase equilibria: a Hildebrand parameter needed for phase separation or miscibility cannot be specified without specifying V_1.

Interchange energy density Equation (B18) works well for nonpolar systems for which Eq. (B17) is a good description of the enthalpic component of the interaction parameter. The geometric mean assumption of regular solution theory is not appropriate for polar systems, and better models include an extra term describing the interchange energy density for the solvent–polymer pair. For example

$$\chi = \chi_S + \frac{V_1 A_{12}}{RT} \tag{B19}$$

with

$$A_{12} = \delta_1^2 + \delta_2^2 - 2 \times l_{12}\delta_1\delta_2 \tag{B20}$$

where l_{12} characterizes the intermolecular forces between molecules (rather than using the geometric mean assumption). Equation (B20) allows the modeling of specific interactions between components 1 and 2. Mixed solvents can be treated as a single solvent by determining the solubility parameter of the solvent mixture, and then using this value in Eq. (B18). If both the solvents and the polymers interact, the description is more complicated. An alternative definition of A_{12} uses the two-component solubility parameter (Ref. 25)

$$A_{12} = (\delta_{1d} - \delta_{2d})^2 + (\delta_{1p} - \delta_{2p})^2 \tag{B21}$$

The Hansen parameters may also be used to model A_{12}.

Several recent theories for polymer solution thermodynamics include entropic, enthalpic and free-volume contributions to the free energy of mixing. The free-volume contributions modify the entropic components, and have the opposite temperature dependence from the combinatorial term, helping to explain the lower critical solution temperature. Since Eq. (B18) assumes a constant value for the entropic component, it may not be valid over large temperature ranges. However, Eq. (B18) will predict the upper critical solution temperature, and, from this standpoint, is adequate for a number of phase equilibria applications near this condition.

The Lattice Fluid model (170) can be used to predict the solubilities of hydrocarbon and chlorinated hydrocarbons in nonpolar polymers. Three-dimensional solubility parameters can be used to provide an empirical correction to the geometric mean approximation (171). This correction predicts the solubility of polar and nonpolar solvents in polymers using only the pure component equation-of-state and solubility parameters.

Guide to polymer–solvent miscibility A region of solubility has been characterized by the distance between solvent and solute coordinates (Ref. 14)

$$R_{ij} = \left(4(\delta_{1d} - \delta_{2d})^2 + (\delta_{1p} - \delta_{2p})^2 + (\delta_{1h} - \delta_{2h})^2\right)^{1/2} \tag{B22}$$

A more general definition of the region of solubility is

$$R_{ij} = \delta_1 - \delta_2 = (a(\delta_{1d} - \delta_{2d})^2 + b(\delta_{1p} - \delta_{2p})^2 + b(\delta_{1h} - \delta_{2h})^2)^{1/2} \tag{B23}$$

where a and b are empirical weighing factors. If the distance between the solvent and the solute Hansen coordinate position exceeds R_{ij}, the two components are not soluble, or swelling is less than expected. R_{ij} reduces the need for three-dimensional plots. Some investigators have used two-dimensional plots for polar and hydrogen bonding terms, but the technique may be misleading for materials with large dispersion contributions. Barton (12) gives a number of models and contour map examples. As mentioned previously, Eqs. (B17)–(B19) suggest that the solvent molar volume can have a significant effect on miscibility.

Zeller (131) reviewed graphical three-dimensional solubility parameter estimation methods (12,14,49,55,172,173) as applied to solvent swelling of crosslinked elastomers. In general, the graphical method (Eqs. B22 and B23) does not account for the known influence of molar volume and crosslink density of solubility, and incorrectly assumes a linear relationship between the solubility parameter difference and solubility. An improved method used the Flory–Rehner equation to modify the interaction parameter for the effects of crosslink density (132).

Guide to polymer–polymer miscibility In many polymer–polymer systems, miscibility can be predicted by comparing the solubility parameters (139). The following table proposes misciblity guidelines. Polymer–polymer miscibility is enhanced when hydrogen bonding is present.

TABLE OF MISCIBILITY GUIDELINES[a]

Intermolecular interaction	Polymer blend example	Critical value of the interaction parameter, χ_{crit}	Upper limit of the non-hydrogen bonded solubility parameter difference, $\Delta\delta$ (MPa$^{1/2}$)
Dispersive forces only	Polyisoprene–Poly-(vinylethylene)	<0.002	<0.02
Dipole–dipole interactions	Poly(methyl methyacrylate)–poly(ethylene oxide)	0.002–0.001	0.2–1.0
Weak hydrogen bonds	Poly(vinyl chloride)–polycaprolactone	0.02–0.2	1.0–2.0
Moderate hydrogen bonds	Poly(vinyl phenol)–poly(vinyl acetate)	0.2–1.0	2.0–5.0
Strong hydrogen bonds	Poly(vinyl phenol)–poly(vinyl methyl ether	1.0–1.5	5.0–6.0

[a] Ref. 139.

C. SOLUBILITY PARAMETER MEASUREMENTS, CALCULATIONS, AND CORRELATIONS

Solubility parameters can be determined by direct measurements, indirect calculations, or correlations with other physical parameters. The solubility parameters of solvents usually can be determined directly by measuring the energy of vaporization. The solubility parameters of polymers can only be determined indirectly and may be affected by variations in their chemical constitutions, i.e., the number of crosslinks and the distribution of chain branches or substitutive groups along the polymer backbone. The methods presented in this section can be used to develop correlations of solubility parameters with other physical properties for specific commercial polymer products or to estimate the solubility parameters of new polymers.

1. Solvents

Calculation of the solubility term (δ) by relating the enthalpy of vaporization to the energy of vaporization Equation (B8) can be used to calculate ΔE_i^v when ΔH_i^v is available. The molar volume of the solute is needed to complete the calculation of δ, using Eq. (B3). This is the most direct and accurate method of determining the solubility parameter. However, δ's determined in this way may not give the best prediction of solution behavior. The solubility parameter values in Tables 7–9 reflect the solvent's behavior in a variety of systems.

Correlations Both the enthalpy of vaporization and the molar volume of a solvent can be estimated from correlations. When ΔH_i^v is known at the normal boiling point, it can be converted to the appropriate value at a second temperature using (126)

$$\frac{\Delta H_i^v(T_2)}{\Delta H_i^v(T_1)} = \left(\frac{T_c - T_2}{T_c - I_1}\right)^{0.38} \qquad \text{(C1)}$$

This corresponding state-type procedure gives estimates within 2% of experimental values over a wide range of temperatures (13). Hildebrand and Scott (59) proposed an empirical correlation between ΔH_i^v at 25°C and the normal boiling point, T_b:

$$\Delta H_i^v(298K) = 0.2950 + 23.6\,T_b + 0.020\,T_b^2 \qquad \text{(C2)}$$

with enthalpy units of kcal/mol. Lawson (67) suggests different coefficients to include fluorocarbon liquids. The Clausius–Clapeyron equation can be applied if vapor pressure data are available. Eq. (C2) is reasonably accurate only for liquids that are not hydrogen bonded. The Hildebrand parameter calculated by Eq. (C2) should be adjusted as follows for different solvents (24): add 1.4 (cal/cm^3)$^{1/2}$ for alcohols, add 0.6 (cal/cm^3)$^{1/2}$ for esters, and add 0.5 (cal/cm^3)$^{1/2}$ for ketones if the boiling point is less than 100°C. Jayasri and Yaseen (64) suggest adding 1.7 (cal/cm^3)$^{1/2}$ for alcohols.

Solvent molar volumes are available or can be calculated by group molar volume methods at 25°C (35,163–165). The molar volume for solids at 25°C can be extrapolated from liquid state values (the liquid is assumed to be subcooled).

Thermodynamic coefficients The internal pressure, π, is defined as (Ref. 88)

$$\pi = \frac{\partial E}{\partial V} = T\beta - P \qquad \text{(C3)}$$

where β is the constant volume thermal pressure coefficient (the ratio of the coefficient of thermal expansion, α, to the isothermal compressibility, κ). Since the external pressure is usually small with respect to $T\beta$, the internal pressure is approximated by

$$\pi = T\beta = T\frac{\alpha}{\kappa} = T\left(\frac{\partial P}{\partial T}\right) \qquad \text{(C4)}$$

The Hildebrand parameter is the square root of the internal pressure. Eq. (C4) provides a method for scaling the Hildebrand parameter with temperature. This equation also provides a method for the direct estimation for δ of polymers; α and κ are measurable when ΔH_i^v is not meaningful (B7). The thermal pressure coefficient (C4) can be evaluated from vapor-pressure data and is easier to apply than the Clausius–Clapeyron equation. For high pressure applications, such as phase equilibria in reverse osmosis membranes, the external pressure term in Eq. (C3) may not be negligible. Solubility parameters generally decrease with increasing pressure.

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van der Waals gas constant Tables are available in many Handbooks for the van der Waals correction constants to the ideal gas law, a and b, where a has units of l^2/atm. For some liquids, these values may be at hand when other data are not available. They can be used to check Hildebrand parameter values obtained from other sources.

$$\delta = 1.2\frac{\sqrt{a}}{V} \tag{C5}$$

The form of Eq. (C5) can be obtained by substituting the van der Waals equation of state into Eq. (C3).

Critical pressure The solubility parameter is related to the critical pressure, P_c of a substance through the empirical equation

$$\delta = 1.25\,P_c^{1/2} \tag{C6}$$

where the critical pressure is expressed in atmospheres. Equation (C6) is not very accurate, but is simple to apply when critical pressure data are available.

Surface tension Michaels (83) has shown that the surface tension can be related to the cohesive energy density:

$$\frac{\Delta E_i^v}{V_i} = A\left(\frac{1}{V_i}\right)^{1/3}\gamma_L \tag{C7}$$

where γ_L is the surface tension and A is a constant. Koenhen and Smolders (65) correlated surface tension and two Hansen parameters:

$$\delta_d^2 + \delta_p^2 = 13.8\left(\frac{1}{V_i}\right)^{1/3}\gamma_L \tag{C8}$$

δ_h is probably not related to the liquid–vapor interfacial energy as these interactions do not involve breaking hydrogen bonds. Eq. (C8) does not describe cyclic compound, acetonitrile, carboxylic acids, polyfunctional alcohols, and other polar compounds well. Hildebrand and Scott (59) have proposed a different equation, which has been discussed by Lee (68).

Index of refraction The dispersive Hansen parameter can be related to the index of refraction, n_D (65,105).

$$\delta_d = 9.55\,n_D - 5.55 \tag{C9}$$

The interaction energy between nonpolar molecules should depend on polarizability (London dispersion forces) and, therefore, on the index of refraction.

Dipole moment Hansen and Skaarup (54) related the polar Hansen parameter to the dielectric constant, ε, and the dipole moment, μ:

$$\delta_p^2 = \frac{12108}{V^2}\frac{\varepsilon - 1}{2\varepsilon + n_D^2}(n_D^2 + 2)\mu^2 \tag{C10}$$

Beerbower and Dicky (14) proposed an empirical relationship:

$$\delta_p^2 = 9.5\frac{\mu}{V_i^{1/2}} \tag{C11}$$

Kauri butanol values Proprietary hydrocarbon solvents are usually mixtures with boiling ranges and unknown molecular weights. Solubility parameter values may be estimated from Kauri butanol values (ASTM Method D1133-54T) using the equation

$$\delta = 6.3 + 0.03\,\mathrm{KB} \tag{C12}$$

2. Polymers

Hildebrand parameters cannot be calculated for polymers from heat of vaporization data because of their nonvolatility. Indirect methods are described below. The solubility parameter values in Table 10 may only be representative of a given polymer since variations in compositions can lead to changes in δ.

2.1. Indirect Measurements

Solvency testing (screening procedure) The classic method for determining solubility parameter of a commercial polymer is solvency testing, or the solvency screening procedure. This technique compares polymer solubility in solvent groups with different hydrogen bonding characteristics (poor, moderate and strong). The midpoints of the polymer's solubility range may be used as single-valued quantities for some purposes, but may not agree with values determined by other methods (43). A gram or two of solid polymer is placed in a test tube and an approximate amount of a selected solvent is added such that the final solution would have about the correct solid content for the expected commercial use, e.g., 50% for alkyds, 20% for vinyls, etc. The exact amount is often unimportant, except for poor solvents. A typical phase diagram for binary polymer–solvent systems may show upper and lower critical solution temperatures. The one-phase region expands away from the UCST and LCST points, which often occur in the range of 20–80 wt.% polymer. The usual purpose of these experiments is to find good solvents for commercial product formulation, and this screening procedure will help identify such solvents. The mixture may be warmed and stirred to speed up solution, but it should be cooled and observed at room temperature. The resulting mixture should be a single phase, clear and free of gel particles or cloudiness, otherwise the polymer is judged insoluble. The solvents to be used are selected from Table 1.

This grouping of solvents has been selected so that the Hildebrand parameter values increase by reasonably constant steps within each hydrogen bonding class. The object of using these solvent spectra is to establish a solubility parameter range for a polymer rather than a single-valued number. This range has the advantage of showing the difference, $(\delta_1 - \delta_2)^2$ (see Eqs. B13, B14 and

B18), which can be tolerated between the solubility values of the polymer and solvent for miscibility. Van Dyk et al. (120) have shown that the molar volume improves the correlation between solvency and the solubility parameters. A better measure of solubility might be the group, $V_1(\delta_1 - \delta_2)^2$.

In carrying out the procedure, it is convenient to select the first trials about 1/2 and 2/3 of the way down the column; for example, in the poorly hydrogen bonded group, toluene and nitroethane would be chosen. If the polymer is soluble in both, there is no need to try intermediate solvents because experience has shown that the polymer will be soluble in every case. The solvents at the end of the spectrum should be tried next. If the polymer is soluble in one but not both of the initial trials, the third trial should be half-way between the two. By successive choices, sets of two adjacent solvents will be found, one of which dissolves the polymer and one that does not. The parameter values of the solvents which do dissolve the polymer mark the ends of the range. The procedure is repeated for the other two hydrogen bonding classes.

Osmotic pressure Fedors (35) used the osmotic pressure of polymer solutions to determine solubility parameters.

Swelling values Another method for measuring the solubility parameter of polymers is to prepare a sparsely crosslinked sample and immerse it in a series of liquids of varying δ (166,167). The crosslinked material will swell to varying degrees, with the maximum amount of swelling occurring when the solvent has the same Hildebrand parameter as the polymer. The amount of swelling can be measured by length, weight, or volume changes. By inference, the soluble, uncrosslinked materials has the same value. An example of a crosslinked sample is styrene polymerized with 1% divinyl benzene.

Turbidity Polymer can be precipitated from dilute solution by adding a non-solvent. The cloud point defines the onset of two phases. The enthalpic component of the interaction parameter, χ_H, can be related to the solubility parameter difference between the solvent and the polymer (Eq. B17). Two different non-solvents are used: one having a solubility parameter above that of the solvent, and another having a solubility parameter below that of the solvent. The enthalpic components of the interaction parameter for each phase are equal at the cloud point, which can be used to measure the solubility parameter of the polymer (116). The two expressions for χ_H are

$$\frac{V_{ml}(\delta_2 - \delta_{ml})^2}{RT} = \frac{V_{mh}(\delta_2 - \delta_{mh})^2}{RT} \qquad \text{(C13)}$$

where V_{ml} and V_{mh} represent the molar volumes at the cloud points of the solvent-lower solubility parameter nonsolvent and solvent-higher solubility parameter nonsolvent, respectively. δ_{ml} and δ_{mh} are the solubility parameters of the mixed solvents. The mixture properties are calculated using

$$\delta_m = \phi_1\delta_1 + \phi_3\delta_3 \qquad \text{(C14)}$$

$$V_m = \frac{V_1V_3}{\phi_1V_3 + \phi_3V_1} \qquad \text{(C15)}$$

where the subscripts, 1 and 3, refer to the solvent and the nonsolvent. Eq. (C13) is simplified to determine the solubility parameter of the polymer:

$$\delta_2 = \frac{(\sqrt{V_{ml}}\delta_{ml} + \sqrt{V_{mh}}\delta_{mh})}{(\sqrt{V_{ml}} + \sqrt{V_{mh}})} \qquad \text{(C16)}$$

The volume fraction of the nonsolvent at the cloud point is used to compute the solvent mixture solubility parameter and molar volume. Cloud point experiments are done for a series of solvents with the two nonsolvents, generating a set of points, (δ_1, δ_2). The intersection of the line defined by this set of points with the line, $\delta_1 = \delta_2$, determines the polymer's solubility parameter.

Specific volume The specific volume of polymers varies with the solvent. Good solvents give higher values of the specific volume while poor solvents give lower values. A plot of the polymer specific volume as a function of solubility parameter gives a maximum value, which is taken to be the solubility parameter of the polymer. High precision density measurements at carefully controlled temperatures are needed for this method (168). The partial specific volume is defined as

$$\bar{V}_i = \left.\frac{\partial V}{\partial c_i}\right|_{T,p,i\neq j} \qquad \text{(C17)}$$

The specific volume of a nonideal two-component system is

$$V_{spec} = \phi_1\bar{V}_1 + \phi_2\bar{V}_2 \qquad \text{(C18)}$$

where $\bar{V}_2$ is the rate of change in volume of the solution when a very small amount of polymer is added. As the solvent volume fraction goes to one, the partial molar volume of solvent is constant and Eq. (C18) becomes

$$V_{spec} = \bar{V}_{1(c_2=0)} + \phi_2\bar{V}_2 \qquad \text{(C19)}$$

The maximum of the polymer partial specific volume is estimated by fitting a quadratic to the data (Ref. 142):

$$\bar{V}_2 = \bar{V}_{2,max} - A(\delta_1 - \delta_2)^2 \qquad \text{(C20)}$$

It is possible to estimate the polymer solubility parameter with only two reference solvents (168), but more reliable values are found by using a range of solvents.

Intrinsic viscosity A number of researchers have used intrinsic viscosity to estimate Hildebrand parameters (74).

Flory (37) related intrinsic viscosity to polymer molecular weight and the chain-expansion factor. The chain-expansion factor can, in turn, be related to the polymer–solvent interaction parameter using the Flory–Huggins theory. Maximum coil extension should occur in solvents near the polymer's solubility parameter. A variety of models can be used to relate the interaction parameter to Hildebrand parameters (19,80,115,167–169). These equations are quadratic (Eq. C21) or take the form of a gaussian curve (Eq. C22):

$$[\eta] = [\eta]_{max} - A(\delta_1 - \delta_2)^2 \quad \text{(C21)}$$

$$[\eta] = [\eta]_{max}\exp(-A(\delta_1 - \delta_2)^2) \quad \text{(C22)}$$

where $[\eta]$ is the intrinsic viscosity, $[\eta]_{max}$ the maximum intrinsic viscosity, and A the constant. These researchers have shown that Eq. (C14) gives a good correlation between solvency and Hansen parameters for methacrylate polymers.

Inverse phase gas chromatography This method has been used by a number of investigators to measure infinite dilution weight fraction activity coefficients (6,29–31,63,71,72,84,90,91,113). These coefficients can be related to Hildebrand parameters by using a thermodynamic theory for polymer solutions, such as Flory–Huggins theory. The polymer is the stationary phase in a gas chromatography column. Both binary and multicomponent equilibria (46,99,100) can be studied using this method. Chromatographic techniques have the advantage of rapid measurement of thermodynamic values once the columns have been made. The solubility parameter can be related to the specific retention volume of the solvent on the column. Both V_i and ΔH_i^v must be known at the temperature of the column. Molar volumes for the solvents can be determined by using literature density equations or generating equations from density data. Values for the enthalpy of vaporization can be determined at the experimental temperature (71).

The inverse phase gas chromatography method has the advantage of providing values for the infinite dilution solubility parameter, δ_i^∞, over a range of temperatures. This is particularly valuable for the prediction of phase equilibria at elevated temperatures. The value of δ_i^∞ at 25°C can be estimated by using the expected temperature dependence for χ (Eq. B18) of

$$\chi = \alpha + \frac{\beta}{T} \quad \text{(C23)}$$

One potential problem with this technique is that χ is known to be a function of concentration and the polymer Hildebrand parameter is determined at infinite dilution of solvent. For a number of binary systems, the change in χ with solvent weight fraction is the largest as $\omega \to 0$. The concentration dependence of the interaction parameter can be modeled using methods given in the chapter on interaction parameters in this Handbook.

2.2. Correlation Methods

Refractive index Koenhen and Smolders (65) have predicted dispersive Hansen parameters from refractive index measurements of polymers. Wu (128) has suggested an effective cross-sectional area to relate the cohesive energy density and surface tension

$$\delta_d^2 = A\left(\frac{n_s}{V_{i,s}}\right)^{1/3}\gamma_s^d \quad \text{(C24)}$$

where n_s is the number of atoms in a segment, $V_{i,s}$ the molar volume of a segment, and γ_s^d the dispersion contribution to the free surface energy of the polymer.

Dipole moment Equation (C10) has been applied to polymers by Koenhen and Smolders (65). The dipole moments of polymers are between 70% and 90% of those of the corresponding monomer units.

Hydrogen-bonding parameter Hansen and Beerbower (55) compiled enthalpy data for hydrogen bonding groups. The following values are suggested:

Group	Cohesive energy, E_h, (kJ/mol)	Refs.
Alcohol	20.9	–
Amide	16.3	83
Ester	5.2	54
Nitrile	2.1	54
Ether	2.3	54
Monochloro substituent	0.4	54
Phenylene ring	0.4	54

The hydrogen-bonding parameter is given by

$$\delta_h^2 = \frac{E_h}{V_i} \quad \text{(C25)}$$

Group contribution methods These methods have been used to estimate the solubility parameter (17,20,28,33,35,58,60,61,96,112,121,122). van Krevelen (123), Fedors (35), and Barton (12) have reviewed these techniques and given tables of group values. The molar volume of solvents and polymers can also be estimated by group contribution techniques (108).

The sets of group constants of Small (112), Hoy (61) van Krevelen (121) and van Krevelen and Hoftyzer (122) seem to be most comprehensive. Table 2 gives the group molar attraction constants at 25°C. Small's values were derived from measurements of the heat of vaporization. Hoy's values were derived from vapor pressure measurements. The group contribution values of van Krevelen and Hoftyzer are based on cohesive energy data of polymers.

The group contribution techniques are based on the assumption that the contributions of different functional groups to the thermodynamic property are additive. The energy of vaporization of a solvent or polymer is

$$\Delta E_i^v = \sum_j n_j \Delta e_j \quad \text{(C26)}$$

where Δe_j is the energy of vaporization contribution of group j, and n_j the number of groups of type j in the molecule. The solubility parameter is obtained by combining Eqs. (B3) and (C26):

$$\delta_i = \left(\frac{\Delta E_i^v}{V_i}\right)^{1/2} = \left(\frac{\sum_j n_j \Delta e_j}{V_i}\right)^{1/2} \quad \text{(C27)}$$

Small (112) defined the molar attraction constant as

$$F_j = (\Delta E_{i,j}^v V_{i,j})^{1/2} \quad \text{(C28)}$$

that can be used to calculate the solubility parameter by

$$\delta_i = \left(\frac{\Delta E_i^v V_i}{V_i^2}\right)^{1/2} = \frac{\sum_j F_j}{V_i} = \frac{\rho_i \sum_j F_j}{M_i} \quad \text{(C29)}$$

where ρ_i is the polymer density and M_i is the polymer molecular weight. δ_i can be evaluated for polymer repeating group by using group contribution calculations for the molar volume and the cohesive energy density or molar attraction constant. Table 2 gives sets of molar attraction constants and the energy of vaporization provided by several different authors. It is preferrable to use parameters from only one set when determining the solubility parameter of a repeating unit. Table 3 gives the cohesive energy densities and group molar volumes determined by Fedors. This set may give less accurate estimates than those in Table 2, but it has value because it is more comprehensive and can be applied to more systems.

Hansen parameters The terms in Eq. (B11) can be estimated by group contribution methods. In general, the resulting factors are known less accurately than the group molar attraction constants or energy of vaporizations. The interaction of structural groups within molecules may not follow simple additive rules. However, the estimate of Hansen parameters can be very useful. Under the method of Hoftyzer and van Krevelen (Table 4), the terms are estimated as

$$\delta_d = \frac{\sum F_{di}}{V}$$
$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V} \quad \text{(C30)}$$
$$\delta_h = \sqrt{\frac{\sum E_{hi}}{V}}$$

The dispersive Hansen parameter treats the molar attraction constants as additive. The polar Hansen parameters also are additive, unless more than one polar group is present. Methods for treating additional polar groups are given in the last three rows of Table 4: additional polar groups do not add linearly to the polar Hansen term. The molar attraction constant is not applied to the hydrogen-bonding Hansen parameter. Rather, a hydrogen bonding energy, E_{hi}, is used.

Hoy (178–179) has an alternative group contribution method (Table 5). It includes a molar attraction function, $F_{t,i}$ a polar component of this function, $F_{p,i}$, the molar volume of the solvent or polymer structural unit, the Lyderson correction for solvent non-ideality, $\Delta_{T,i}$, and a similar correction for polymer non-ideality, $\Delta_{T,i}^{(P)}$.

Bicerano (164) and Porter (165) have developed new group contribution techniques for a wide variety of polymer properties. These approaches consider how the different functional groups are connected in the molecule or in the polymeric repeating unit. Bicerano's method uses Fedor's (35) and van Krevelen's (123,163) group contribution values. Both references provide solubility parameter predictions of a number of polymers.

TABLE 1. SELECTED SOLVENTS FOR USE IN POLYMER SOLVENCY TESTING

Solvent	δ (MPa$^{1/2}$)
POORLY HYDROGEN BONDED	
n-Pentane	14.3
n-Heptane	15.1
Methylcyclohexane	16.0
Solvesso 150	17.4
Toluene	18.2
Tetrahydronaphthalene	19.4
o-Dichlorobenzene	20.5
1-Bromonaphthalene	21.7
Nitroethane	22.7
Acetonitrile	24.1
Nitromethane	26.0
MODERATELY HYDROGEN BONDED	
Diethyl ether	15.2
Diisobutyl ketone	16.0
n-Butyl acetate	17.4
Methyl propionate	18.2
Dibutyl phthalate	19.0
Dioxane	20.3
Dimethyl phthalate	21.9
2,3-Butylene carbonate	24.8
Propylene carbonate	27.2
Ethylene carbonate	30.1
STRONGLY HYDROGEN BONDED	
2-Ethyl hexanol	19.4
Methyl isobutyl carbinol	20.5
2-Ethyl butanol	21.5
n-Pentanol	22.3
n-Butanol	23.3
n-Propanol	24.3
Ethanol	26.0
Methanol	29.7

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TABLE 2. GROUP CONTRIBUTIONS TO COHESIVE ENERGY DENSITY

Group	F [MPa$^{1/2}$ cm^3/mol]		ΔE_i^v(J/mol)	
	Small (112)	van Krevelen (121)	Hoy (61)	van Krevelen and Hoftyzer (163)
2.1. CARBON-CONTAINING GROUPS				
$-CH_3$	437	420	303	9630
$\rangle CH_2$	272	280	269	4190
$\rangle CH-$	57	140	176	420
$\rangle C\langle$	−190	0	65	−5580
$=CH_2$	388	–	259	–
$=CH-$	277	222	249	–
$=C\langle$	39	82	173	–
−CH=(aromatic)	–	–	240	–
−C=(aromatic)	–	–	201	–
$-CH(CH_3)-$	495	560	(479)	(10060)
$-C(CH_3)_2-$	685	841	(672)	(13700)
−CH=CH−	454	444	497	10200
−C=CH−	265	304	421	4860
CH_3 H, $C=C$	(704)	724	(725)	(14500)
H−C≡C−	583	–	–	–
−C≡C−	454	–	–	–
Cyclopentyl	–	1380	1300	–
Cyclohexyl	–	1660	1470	–
Phenyl	1500	1520	(1400)	31000
p-Phenylene	1350	1380	(1440)	25140
Naphthyl	2340	–	–	–
2.2. OXYGEN-CONTAINING GROUPS				
−O−, ether	143	255	235	6290
−O−, epoxide	–	–	360	–
−OH	–	754	462	–
−OH, aromatic	–	–	350	–
−(C=O)−	562	685	538	–
−(C=O)−O−	634	511	688	13410
−(C=O)−OH	–	651	(998)	–
−O−(C=O)−O−	–	767	(904)	–
−(C=O)−O−(C=O)−	–	767	1160	–
2.3. NITROGEN-CONTAINING GROUPS				
$-NH_2$	–	–	464	–
−NH−	–	–	368	–
$-N\langle$	–	–	125	–
−CH−CN	(896)	1120	(901)	25420
−CN	839	982	725	25000
−(C=O)−NH−	–	1290	(906)	60760
−O−(C=O)−NH	–	1480	(1040)	–
−N=C=O	–	–	734	–
2.4. OTHER GROUPS				
−H	164–205	140	−103 (acidic dimer)	–
−S−	460	460	428	8800
−SH	644	–	–	–
−F	(250)	164	84	4470
−Cl (primary)	552	471	420	12990
−Br (primary)	695	614	528	15500
−I	870	–	–	–
$-CF_2-$	307	–	–	–
$-CF_3$	561	–	–	–
−O−N=O	900	–	–	–
$-NO_2$	900	–	–	–
$-PO_4$	1020	–	–	–
−Si−	−77	–	–	–

TABLE 2. *cont'd*

Group	F [MPa$^{1/2}$ cm^3/mol] Small (112)	F [MPa$^{1/2}$ cm^3/mol] van Krevelen (121)	ΔE_i^v(J/mol) Hoy (61)	ΔE_i^v(J/mol) van Krevelen and Hoftyzer (163)
2.5. STRUCTURAL FEATURES				
Conjugation	41–61	–	48	–
cis	–	–	−15	–
trans	–	–	−28	–
Ring, 4 member	–	–	159	–
5 member	215–235	–	43	–
6 member	194–215	–	−48	–
Subscription, ortho	–	–	20	–
meta	–		14	–

TABLE 3. CONTRIBUTIONS TO E_{coh} AND V[a]

Group	E_{coh} (J/mol)	V (cm^3/mol)
$-CH_3$	4710	33.5
$\diagdown CH_2$	4940	16.1
$\diagdown CH-$	3430	−1.0
$\diagdown C\diagup$	1470	−19.2
$=CH_2$	4310	28.5
$=CH-$	4310	13.5
$=C\diagup$	4310	−5.5
$H-C\equiv$	3850	27.4
$-C\equiv$	7070	6.5
Phenyl	31940	71.4
Phenylene: *o*, *m*, *p*	31940	52.4
Phenyl (trisubstituted)	31940	33.4
(tetrasubstituted)	31940	14.4
(pentasubstituted)	31940	−4.6
(hexasubstituted)	31940	−23.6
Ring closure, 5+ atoms	1050	16.0
3 or 4 atoms	3140	18.0
Conjugation in ring for each double bond	1670	−2.2
Halogen attached to carbon atom with double bond	−20% of E_{coh} of halogen	4.0
$-F$	4190	18.0
−F, disubstituted	3560	20.0
trisubstituted	2300	22.0
$-CF_2-$, perfluoro compounds	4270	23.0
$-CF_3$, perfluoro compounds	4270	57.5
$-Cl$	11550	24.0
−Cl, disubstituted	9630	26.0
trisubstituted	7530	27.3
$-Br$	15490	30.0
−Br, disubstituted	12350	31.0
trisubstituted	10670	32.4
$-I$	19050	31.5
−I, disubstituted	16740	33.5
trisubstituted	16330	37.0
$-CN$	25530	24.0
$-OH$	29800	10.0
−OH, disubstituted or adjacent C atoms	21850	13.0
$-O-$	3350	3.8
−CHO, aldehyde	21350	22.3
$-CO-$	17370	10.8
$-COOH$	27630	28.5
$-COO-$	18000	18.0
$-CO_3-$, carbonate	17580	22.0
$-C_2O_3-$, anhydride	30560	30.0

TABLE 3. *cont'd*

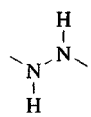
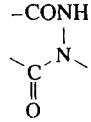
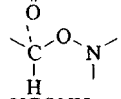
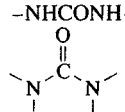
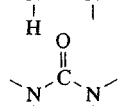
Group	E_{coh} (J/mol)	V (cm^3/mol)
HCOO−, formate	18000	32.5
$-CO_2CO_2-$, oxalate	26790	37.3
$-HCO_3$	12560	18.0
$-COF$	13400	29.0
$-COCl$	17580	38.1
$-COBr$	24150	41.6
$-COI$	29300	48.7
$-NH_2$	12560	19.2
$-NH-$	8370	4.5
$-N\diagup$	4190	−9.0
$-N=$	11720	5.0
$-NHNH_2$	21980	–
$-N(NH_2)-$	16740	16.0
	16740	16.0
$-N_2$, diazo	8370	23
$-N=N-$	4190	–
$\diagdown C-N=N-C\diagup$	20090	–
$-N=C=N-$	11470	–
$-N\equiv C$	18840	23.1
$-NF_2$	7660	33.1
$-NF-$	5070	24.5
$-CONH_2$	41860	17.5
$-CONH-$	33490	9.5
	29510	−7.7
	27630	11.3
HCONH−	43950	27.0
$-NHCOO-$	26370	18.5
$-NHCONH-$	50230	–
	41860	–
	20930	−14.5
NH_2COO-	37000	–
$-NCO$	28460	35.0
$-ONH_2$	19050	20.0

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TABLE 3. *cont'd*

Group	E_{coh} (J/mol)	V (cm^3/mol)
	25120	11.3
–CH=NOH	25120	24.0
$-NO_2$, aliphatic	29300	24.0
$-NO_2$, aromatic	15360	32.0
$-NO_3$	20930	33.5
$-NO_2$, nitrate	11720	33.5
$-NHNO_2$	39770	28.7
–NNO–	27210	10.0
–SH	14440	28.0
–S–	14150	12.0
$-S_2-$	23860	23.0
$-S_3-$	13400	47.2
	39140	–
SO_3	18840	27.6
SO_4	28460	31.6
$-SO_2Cl$	37070	43.5
–SCN	20090	37.0
–NCS	25120	40.0
P	9420	– 1.0
PO_3	14230	22.7
PO_4	20930	28.0
PO_3–OH	31810	32.2
Si	3390	0
SiO_4	21770	20.0
B	13810	– 2.0
BO_3	0	20.4
Al	13810	– 2.0
Ga	13810	– 2.0
In	13810	– 2.0
Tl	13810	– 2.0
Ge	8080	– 1.5
Sn	11300	1.5
Pb	17160	2.5
As	12980	7.0
Sb	16330	8.9
Bi	21350	9.5
Se	17160	16.0
Te	20090	17.4
Zn	14480	2.5
Cd	17790	6.5
Hg	22810	7.5

[a] Ref. 35.

TABLE 4. SOLUBILITY PARAMETER I: COMPONENT GROUP CONTRIBUTIONS[a]

Structural Group	F_{di} (J$^{1/2}$ cm$^{3/2}$/mol)	F_{pi} (J$^{1/2}$ cm$^{3/2}$/mol)	E_{hi} (J/mol)
$-CH_3$	420	0	0
	270	0	0
	80	0	0
	– 70	0	0
$=CH_2$	400	0	0
=CH–	200	0	0
	70	0	0
	1620	0	0
	1430	110	0
 (*o*, *m*, *p*)	1270	110	0
–F	(220)	-	-
–Cl	450	550	400
–Br	(550)	-	-
–CN	430	1100	2500
–OH	210	500	20000
–O–	100	400	3000
–COH	470	800	4500
–CO–	290	770	2000
–COOH	530	420	10000
–COO–	390	490	7000
HCOO–	530	–	–
$-NH_2$	280	–	8400
–NH–	160	210	3100
	20	800	5000
$-NO_2$	500	1070	1500
–S–	440	–	–
$=PO_4-$	740	1890	13000
Ring	190	–	–
One plane of symmetry	–	0.50 ×	
Two planes of symmetry	–	0.25 ×	–
More planes of symmetry	–	0 ×	0 ×

[a] Ref. 163.

TABLE 5. SOLUBILITY PARAMETER II: COMPONENT GROUP CONTRIBUTIONS[a]

Group	F_{ti} ((J cm^3)$^{1/2}$/mol)	F_{pi} ((J cm^3)$^{1/2}$/mol)	V_i (cm^3/mol)	$\Delta_{Ti}{}^*$	$\Delta_{Ti}^{(P)}$
$-CH_3$	303.5	0	21.55	0.023	0.022
	269.0	0	15.55	0.020	0.020
	176.0	0	9.56	0.012	0.013
	65.5	0	3.56	0	0.04
$=CH_2$	259	67	19.17	0.018	0.019
=CH–	249	59.5	13.18	0.018	0.0185
	173	63	7.18	0	0.013
$CH_{aromatic}$	241	62.5	13.42	0.011	0.018
$C_{aromatic}$	201	65	7.42	0.011	0.015
–HC=O	600	532	23.3	0.048	0.045

TABLE 5. *cont'd*

Group	$F_{t,i}$ ((J cm^3)$^{1/2}$/mol)	$F_{p,i}$ ((J cm^3)$^{1/2}$/mol)	V_i (cm^3/mol)	$\Delta_{T,i}{}^*$	$\Delta_{T,i}^{(P)}$
–CO–	538	525	17.3	0.040	0.040
–COOH	565	415	26.1	0.039	0.039
–COO–	640	528	23.7	0.047	0.050
–CO–O–CO–	1160	1160	41.0	0.086	0.086
–CN	725	725	23.1	0.060	0.054
–N=C=O	736	8.2	25.9	0.054	0.054
–N(HCO)–	1020	725	35.8	0.062	0.055
$-CONH_2$	1200	900	34.3	0.071	0.084
–CONH–	1131	895	28.3	0.054	0.073
–OCONH–	1265	890	34.8	0.078	0.094
–OH→H-bonded	485	485	10.65	0.082	0.034
–OH, primary	675	675	12.45	0.082	0.049
secondary	591	591	12.45	0.082	0.049
tertiary	(500)	(500)	12.45	0.082	0.049
phenolic	350	350	12.45	0.031	0.006
–O–, ether	235	216	6.45	0.021	0.018
acetal	236	102	6.45	0.018	0.018
epoxide	361	156	6.45	0.027	0.027
$-NH_2$	464	464	17.0	0.031	0.035
–NH–	368	368	11.0	0.031	0.275
$-N\diagup\diagdown$	125	125	12.6	0.014	0.009
–S–	428	428	18.0	0.015	0.032
–F	845	73.5	11.2	0.018	0.006
–Cl, primary	419.5	307	19.5	0.017	0.031
secondary	426	315	19.5	0.017	0.032
aromatic	330	81.5	19.5	0.017	0.025
$\diagup$Cl $\diagdown$Cl	705	572	39.0	0.034	0.052
–Br, aliphatic	528	123	25.3	0.010	0.039
aromatic	422	100	25.3	0.010	0.031
Base value, B	277				
Ring, non-aromatic 4-member	159	203	–	0	0.012
5-member	43	85	–	0	0.003
6-member	–48	61	–	0	–0.0035
7-member	92	0	–	0	0.007
Conjugation, isomerism	47.5	–19.8	–	0	0.0035
cis	–14.6	–14.6	–	0	–0.001
trans	–27.6	–27.6	–	0	–0.002
Aromatic substitution, ortho	20.2	–13.3	–	0	0.0015
meta	13.5	–24.3	–	0	0.001
para	83	–34.0	–	0	0.006

[a] Ref. (178–179).

TABLE 6. EQUATIONS TO BE USED FOR HOY'S SYSTEM[a]

Formulae	Solvents	Amorphous polymers
Additive molar functions	$F_t = \sum n_i F_{t,i}$	$F_t = \sum n_i F_{t,i}$
	$F_p = \sum n_i F_{p,i}$	$F_p = \sum n_i F_{p,i}$
	$V = \sum n_i V_i$	$V = \sum n_i V_i$
	$\Delta_T = \sum n_i \Delta_{T,i}$	$\Delta_T^{(P)} = \sum n_i \Delta_{T,i}^{(P)}$
Auxiliary equations	$\log \alpha = 3.39 \frac{T_b}{T_{cr}} - 0.1585 - \log V$,	$\frac{\alpha^{(P)} = 777 \Delta_T^{(P)}}{V}$
	T_b = boiling point, T_{cr} = critical temp.	
	$\left(\frac{T_b}{T_{cr}}\right) = 0.567 + \Delta_T - (\Delta_T)^2$,	$\bar{n} = \frac{0.5}{\Delta_T^{(P)}}$
	Lyderson equation	
Expressions for δ and δ-components	$\delta_t = \frac{F_t + B}{V}$; $B = 277$	$\delta_t = \frac{F_t + \frac{B}{\bar{n}}}{V}$; $B = 277$

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TABLE 6. *cont'd*

Formulae	Solvents	Amorphous polymers
	$\delta_p = \delta_t\left(\frac{1}{\alpha}\frac{F_p}{F_t + B}\right)^{1/2}$	$\delta_p = \delta_t\left(\frac{1}{\alpha^{(P)}}\frac{F_p}{F_t + B/\bar{n}}\right)^{1/2}$
	$\delta_h = \delta_t\left(\frac{\alpha - 1}{\alpha}\right)^{1/2}$	$\delta_h = \delta_t\left(\frac{\alpha^{(P)} - 1}{\alpha^{(P)}}\right)^{1/2}$
	$\delta_d = (\delta_t^2 - \delta_p^2 - \delta_h^2)^{1/2}$	$\delta_d = (\delta_t^2 - \delta_p^2 - \delta_h^2)^{1/2}$

[a] In the equations given here, F_t is always combined with a Base value, α is the molecular aggregation number, and $\bar{n}$ the number of repeating units per polymer chain segment.

D. SOLUBILITY PARAMETER TABLES

TABLE 7. SOLUBILITY PARAMETERS OF SOLVENTS IN ALPHABETICAL ORDER

Solvent	CAS number	Solubility parameter δ		H-bonding group
		$(MPa^{1/2})$	$(cal/cm)^{1/2}$	
Acetaldehyde	75-07-0	21.1	10.3	m
Acetic acid	64-19-7	20.7	10.2	s
Acetic anhydride	108-24-7	21.1	10.3	s
Acetone	67-64-1	20.3	9.9	m
Acetonitrile	75-07-8	24.3	11.9	p
Acetophenone	98-86-2	21.7	10.6	m
Acetyl chloride	75-36-5	19.4	9.5	m
Acetylmorpholine (*N*)	1696-20-4	23.7	11.6	m
Acetylpiperidine (*N*)	618-42-8	22.9	11.2	s
Acetylpyrrolidine (*N*)	1072-83-9	23.3	11.4	s
Acrolein	107-02-8	20.1	9.8	s
Acrylic acid	79-10-7	24.6	12.0	s
Acrylonitrile	107-13-1	21.5	10.5	p
Allyl acetate	591-87-7	18.8	9.2	m
Allyl alcohol	107-18-6	24.1	11.8	s
Allyl chloride	107-05-1	18.0	8.8	m
Ammonia	7664-41-7	33.4	16.3	s
Amyl acetate (iso)	625-16-1	16.0	7.8	m
(normal)	628-63-7	17.4	8.5	m
(secondary)	626-38-0	17.0	8.3	m
Amyl alcohol	75-85-4	20.5	10.0	s
Amyl alcohol (normal)	71-41-0	22.3	10.9	s
Amylamine (normal)	110-58-7	17.8	8.7	s
Amyl bromide (1-bromopentane)	110-53-2	15.6	7.6	m
Amyl chloride (1-chloropentane)	543-59-9	17.0	8.3	m
Amylene (2-methyl-2-butene)	513-35-9	14.1	6.9	p
Amyl ether (pentyl ether)	693-65-2	14.9	7.3	m
Amyl formate (iso)	110-45-2	16.4	8.0	m
(normal)	638-49-3	17.2	8.5	m
Amyl iodide (1-iodopentane)	628-17-1	17.2	8.4	m
Anethole (*para*)	4180-23-8	17.2	8.4	m
Aniline	65-53-3	21.1	10.3	s
Anthracene	120-12-7	20.3	9.9	p
Apco #18 solvent		15.3	7.5	p
Apco #140 solvent		14.9	7.3	p
Apco thinner		16.0	7.8	p
Aroclor 1248	12672-29-6	18.0	8.8	p
Benzaldehyde	100-52-7	19.2	9.4	m
Benzene	71-43-2	18.8	9.2	p
Benzonitrile	100-47-0	17.2	8.4	p
Benzyl alcohol	100-51-6	24.8	12.1	s
Bicyclohexyl	92-51-3	17.4	08.5	p
Bromobenzene	108-86-1	20.3	09.9	p
1-Bromonaphthalene	90-11-9	21.7	10.6	p
Bromostyrene (*ortho*)	2039-88-5	20.1	9.8	p
1,3-Butadiene	106-99-0	14.5	7.1	p