

CHAPTER 16

Solubility Parameters

W. Zeng, Y. Du, Y. Xue, and H. L. Frisch

Department of Chemistry, State University of New York, Albany, NY 12222

16.1	Cohesive Energy Density and Solubility (Hildebrand) Parameter	289
16.2	Expanded Solubility Parameters	290
16.3	Calculation and Correlations for Solubility Parameters	290
16.4	Polymer-Solvent Interaction Parameter	293
	Acknowledgment	302
	References	302

Solubility parameters provide a simple method of correlating and predicting the cohesive and adhesive properties of materials from a knowledge of the properties of the components only. Particularly for polymers, applications include finding compatible solvents for coating resins, predicting the swelling of cured elastomers by solvents, estimating solvent pressure in devolatilization and reactor equipment [1] and predicting polymer–polymer [2], polymer–binary-solvent [3], random copolymer [4], and multi-component solvent equilibria [5–8].

16.1 COHESIVE ENERGY DENSITY AND SOLUBILITY (HILDEBRAND) PARAMETER

If U is defined as the molar internal energy (the molar potential energy of a material relative to the ideal vapor at the same temperature), then the molar cohesive energy (the energy associated with the net attractive interactions of the material) is defined as $-U$. As presented by Polak [9]:

$$-U =_l \Delta_g U + g \Delta_\infty U, \quad (16.1)$$

where $\Delta_g U$ is the molar vaporization energy and $g \Delta_\infty U$ is the energy required to expand the saturated vapor to infinite volume at constant temperature, that is, the energy necessary to completely separate the molecules.

The stabilizing or cohesive effect in condensed phases can be expressed in terms of the cohesive energy density, defined as

$$c = -U/V, \quad (16.2)$$

where V is the molar volume. Cohesive energy was the basis of the original definition by Hildebrand and Scott [10–12] of

what is now generally called the solubility parameter or Hildebrand parameter:

$$\delta = c^{0.5} = (-U/V)^{0.5}. \quad (16.3)$$

This parameter was intended for nonpolar, nonassociating systems in which $g \Delta_\infty U = 0$ and $-U =_l \Delta_g U$, but the concept has been extended to all types of systems. The dimension of δ is $(\text{cal}/\text{cm}^3)^{0.5} = 2.046 \times 10^3 (\text{J}/\text{m}^3)^{0.5} = 2.046 \text{ MPa}^{0.5}$. The solubility parameter can be considered as the “internal pressure” of the solvent [13–15].

Based on the pioneering work of van der Waals [16] and van Laar [17], the Hildebrand–Scatchard equation was derived on semitheoretical grounds by Scatchard [18,19] and Hildebrand [20–24] and popularized by Hildebrand, Scott, Prausnitz and others [25–37, 10–12]. For a binary mixture, the Hildebrand–Scatchard equation is expressed as

$$\Delta H_m/V_m = (\delta_1 - \delta_2)^2 \phi_1 \phi_2, \quad (16.4)$$

where ΔH_m is the enthalpy change on mixing, V_m the volume of the mixture, ϕ_i the volume fraction of i in the mixture, and δ_i the solubility parameter of the i th component. In general, $(\delta_1 - \delta_2)^2$ must be small for the components to be miscible. Equation (16.4) gives the heat of mixing of regular solutions in which (a) the components mix with no volume change on mixing at constant pressure, (b) the interaction forces act between the center of the molecules and the interaction between a pair of molecules is not influenced by the presence of other molecules, (c) the mixing is random and the distribution is temperature independent, (d) no reaction occurs between the components, and (e) there is no complex formation or special association. These assumptions are not generally valid, but they produce an

equation which has proven valuable both in its own right and as a starting point for other empirical expressions.

16.2 EXPANDED SOLUBILITY PARAMETERS

The solubility parameter describes the enthalpy change on mixing of nonpolar solvents well but does not give uniform results when extended to polar systems. Complete miscibility is expected to occur if the solubility parameters are similar and the degree of hydrogen bonding is similar between the components. Other investigators have decomposed the Hildebrand parameter into several terms, representing different contributions to the energy of mixing. van Arkel [38], Small [39], and Andersen, Prausnitz, and co-workers [12,40–45] divided the total solubility parameter into two main components, defining a nonpolar solubility (δ_λ) and a polar solubility parameter (δ_τ). Although this tends to neglect induction interactions, these may be taken care of by an additional parameter. Polar–nonpolar parameters are related to the Hildebrand parameter by

$$\delta^2 = \delta_\lambda^2 + \delta_\tau^2. \quad (16.5)$$

Here δ_λ can be identified with the dispersive term and δ_τ corresponds to the polar orientational term. This approach has been also applied to polymer solutions [41] and complex formation [46].

Hansen and co-workers [47–68] proposed a practical extension of the Hildebrand parameter method to polar and hydrogen-bonding systems, primarily for use in polymer–liquid interactions. It was assumed that dispersion, polar, and hydrogen-bonding parameters were valid simultaneously, related by Eq. (16.6), with the values of each component being determined empirically on the basis of many experimental observations:

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2, \quad (16.6)$$

where δ_t is Hansen's total solubility parameter, δ_d the dispersive term, δ_p the polar term, and δ_h the hydrogen-bonding term. Hansen's total solubility parameter should be equal to the Hildebrand parameter, although the two quantities may differ for materials with specific interactions when they are determined by different methods. The three component parameters were plotted on a set of three mutually perpendicular axes. The Hansen parameters give improved agreement with data but are still not completely accurate in predicting solution thermodynamics for every system.

Parameters describing and correlating the solvent abilities of liquids have been based on a great variety of chemical and physical properties. Some are measures of solvent basicity, and others are obtained from direct determinations of the solubility of a representative solute in a range of liquids. For example, the solubility of hydrogen chloride in liquids at 10 °C was used in this way by Gerrard and co-workers [69,70] and the resulting solvent basicity scale was compared with other scales by Arnett [71] and by Dack [72].

More direct measures of liquid basicity include the enthalpy of mixing with trichloromethane and with other halogenated hydrogen-bond donors in basic solvents [72,71] and the enthalpy of coordination with antimony trichloride [71,73]. Most of the other numerous scales of “basicity” or “electron donating ability” are single-valued and even more difficult to correlate with each other or with solubility parameters. Although they agree in their general trends, the detailed orders of solvent basicity depend on the system from which the scale is derived [72,74].

16.3 CALCULATION AND CORRELATIONS FOR SOLUBILITY PARAMETERS

16.3.1 Solvents

Solubility parameters can be determined by direct measurement, correlations with other physical parameters, or indirect calculations. The solubility parameters of solvents usually can be determined directly. The following methods can be used to develop correlations between solubility parameters and other physical properties of solvents.

Vaporization Enthalpy

If the enthalpy of vaporization, ΔH , has been determined calorimetrically (or from the temperature dependence of the vapor pressure) at the required temperature, and if this is well below the boiling point of the liquid, the Hildebrand parameter may be evaluated with the assumption that the vapor is ideal:

$$\delta = (\Delta H - RT)^{0.5} / V^{0.5}. \quad (16.7)$$

When the value of the vaporization enthalpy is known at one temperature (commonly at normal boiling point), it is desirable to be able to evaluate it at another temperature. In such procedures for extrapolating volumes or enthalpies, a corresponding state procedure is often used. This is frequently based on the reduced temperature T_r , reduced vapor pressure P_r , and reduced molar volume V_r , defined by

$$T_r = T/T_c, P_r = P/P_c, V_r = V/V_c, \quad (16.8)$$

where the subscript c refers to the values at the critical point. For example, ΔH may be evaluated to within about 2% over a wide range of temperatures, even within a few degrees of T_c by means of the Watson empirical relationship [75–77]:

$$\begin{aligned} \Delta H_2 / \Delta H_1 &= (T_c - T_2)^{0.38} / (T_c - T_1)^{0.38} \\ &= (1 - T_{r,2})^{0.38} / (1 - T_{r,1})^{0.38}. \end{aligned} \quad (16.9)$$

Solvent molar volume are often available or can be calculated by group molar volume methods at 25 °C [76]. The molar volume for solids at 25 °C can be extrapolated from liquid-state values (if the liquid is assumed to be subcooled).

Boiling Point

A simple, convenient method of estimating the vaporization enthalpy is the application of the Hildebrand and Scott equation [12,24,35], which expresses ΔH at 25 °C (ΔH^0) in terms of the normal boiling point T_b :

$$\begin{aligned}\Delta H^0(\text{J mol}^{-1}) = & -12\ 340 + 99.2[T_b(\text{K})] \\ & + 0.084[T_b(\text{K})]^2\end{aligned}\quad (16.10)$$

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 . 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:

$$\delta = 1.2 \frac{a^{1/2}}{V}, \quad (16.11)$$

where a has units of 1² atm.

Surface Tension

Michaels [78] has shown that the surface tension can be related to the cohesive energy density

$$\frac{\rho \Delta_g V}{V_i} = A \left(\frac{I}{V_i} \right)^{1/3} \gamma_L, \quad (16.12)$$

where γ_L is the surface tension, V_i is the molar volume of species i , and A is a constant. Koenhen and Smolders [79] correlated surface tension and two Hansen parameters:

$$\delta_d^2 + \delta_p^2 = 13.8 \left(\frac{I}{V_i} \right)^{1/3} \gamma_L. \quad (16.13)$$

Equation (16.9) does not describe cyclic compounds, acetonitrile, carboxylic acids, polyfunctional alcohols, and other polar compounds as well. δ_h is probably not related to the liquid–vapor interfacial energy; these interactions do not involve breaking hydrogen bonds.

Internal Pressure

The internal pressure is defined as

$$\pi = (\partial U / \partial V)_T. \quad (16.14)$$

Bagley and co-workers [14,15,80,81] and Scigiano [82] utilized the chemical-bond-discriminating property of cohesive and internal pressures to subdivide the Hildebrand parameter in another way. One part corresponding to the physical or nonchemical effects is the volume-dependent Hildebrand parameter, defined by

$$\delta_v^2 = \pi. \quad (16.15)$$

The other component is a residual parameter, arising from chemical effects:

$$\delta_p^2 = (\Delta U - \pi V)/V, \quad (16.16)$$

$$\delta_p^2 \approx \delta_h^2, \delta_v^2 \approx \delta_d^2 + \delta_p^2. \quad (16.17)$$

One advantage of this approach for separation of the component parameters is that it makes use of the thermodynamic quantities π and ΔU , which are fairly readily available for most liquids, in contrast to other empirically determined component solubility parameters. The internal pressure can be measured experimentally by determining the thermal pressure coefficient or the coefficient of expansion and isothermal compressibility, it also can be calculated from other physical properties. Vavruch [83] developed and tested an expression for internal pressure in terms of critical temperature T_c ,

$$\pi (\text{MPa}) = 63.0(1.5T_c - T)/V, \quad (16.18)$$

where V is the molar volume. The mean percentage deviation was 3.8% for 25 selected liquids (excluding alkanes, alkenes, monohydric alcohols, carboxylic acids, water, liquid metals, and probably cryogenic fluids).

Index of Refraction

The dispersive Hansen parameter δ_d can be related to the index of refraction n_D [79,84]:

$$\delta_d = 9.55n_D - 5.55. \quad (16.19)$$

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

Dipole Moment

Hansen and Skaarup [66] related the polar Hansen parameter to the dielectric constant ϵ and the dipole moment μ :

$$\delta_p^2 = \frac{12}{V^2} \frac{108}{2\epsilon + n_D^2} \frac{\epsilon - 1}{(n_D^2 + 2)\mu^2}. \quad (16.20)$$

Beerbower and Dicky [85] proposed an empirical relationship:

$$\delta_p^2 = 9.5\mu/V_i^{1/2}. \quad (16.21)$$

16.3.2 Polymers

Measurements

For polymers, solubility parameters cannot be calculated from heat of vaporization data because of their nonvolatility. Other methods of estimation must be used.

The Internal Pressure P_i

Olabisi and Simha [86] developed one approach to calculate the solubility parameter through the internal pressure, P_i :

$$\delta^2 = P_i = \left(\frac{\partial U}{\partial V} \right)_T \approx T\alpha/\beta, \quad (16.22)$$

where α is the thermal expansion coefficient ($^{\circ}\text{C}^{-1}$) and β is the compressibility (cm^3/cal).

Swelling Data

A method often used for slightly cross-linked polymers [87] and applicable to partially crystalline material such as polyvinyl chloride (PVC) is based on finding the maximum swelling using a series of solvents of varying and known solubility parameters. The assumption is that the interaction and the degree of swelling will be a maximum when the solubility parameter of the polymer matches that of the solvent. This may be inaccurate for systems having opposite polarities or interacting through hydrogen bonding for which the heat of mixing is negative.

Inverse Phase Gas Chromatography

A number of investigations have been performed to measure infinite dilution weight fraction activity coefficients by applying inverse phase gas chromatography [88–97]. These coefficients can be related to solubility 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 [98,99] can be studied using this technique. Values of the enthalpy of vaporization can be determined at the experimental temperature [93]. Chromatographic methods have the advantage of measurement of thermodynamic values once the columns have been made. Both V_1 and ΔH_v^n 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.

Refractive Index

Dispersive Hansen parameters can be predicted from refractive-index measurements of polymers [79]. Wu [100] has suggested an effective cross-sectional area to relate the cohesive energy density and surface tension.

$$\delta_d^2 = A \left(\frac{n_s}{V_{i,s}} \right)^{1/3} \gamma_s^d, \quad (16.23)$$

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

Intrinsic Viscosity

Solubility parameters can also be estimated from intrinsic viscosity. Flory [101] 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. A variety of models can be used to relate the interaction parameter to solubility parameters [87,102,103]; these equations have the form

$$[\eta] = K_I - K_{II} V_i^n \Delta \delta^2, \quad (16.24)$$

where $[\eta]$ is the intrinsic viscosity, K_i are constants, and n is either 1/2 or 1 [104].

Other Methods

The dipole moment has been successfully applied to measure δ_p by Koenhen and Smolders [79]. The dipole moments of polymers are between 70% and 90% of those of the corresponding monomer units. The Hansen hydrogen-bonding parameter δ_h is given by [63]

$$\delta_h^2 = E_h/V_i. \quad (16.25)$$

The solubility parameter can also be calculated through the heat of solution directly [105,106], solution behavior [107,108], and by extrapolation [109].

Group Contribution Methods

Group contribution methods have been applied to the problem of estimating the solubility parameter without physical measurements [110–117,39,118,119]. Small [39] was one of the first to recognize the additive properties of the molar attraction constant F_i , which is defined by

$$F_i = (E_i V_i)^{1/2}, \quad (16.26)$$

where E_i and V_i are the cohesion energy and molar volume of the group being considered. Values of F_i , in units of $\text{cal}^{1/2} \text{cm}^{3/2}$, were obtained by regression analysis for various common structural groups in low-molecular-weight compounds. From the additivity of the F_i values and Eq. (16.3) one obtains:

$$\delta = \rho \frac{\sum_i F_i}{M}, \quad (16.27)$$

where ρ is the density of the polymer, M is the molar mass of the polymer, and the summation is carried over all structural features in the molecule.

The contributions of Hoy [116], Konstam and Feairlieller [120], and Van Krevelen [121] is summarized in Table 16.1. Some values of F_i , from which solubility parameters can be calculated with the aid of Eq. (16.27), are listed.

TABLE 16.1. Group contributions to solubility parameter^a.

Group		<i>F_i</i>	
	Small	van Krevelen	Hoy
-CH ₃	437	420	303
—CH ₂ —	272	280	269
—CH—	57	140	176
—C≡C—	-190	0	65
—CH ₂	388	—	259
—CH—	227	222	249
—C<	39	82	173
—CH=(aromatic)	—	—	240
—C=(aromatic)	—	—	201
—CH(CH ₃)—	495	560	479
—C(CH ₃) ₂ —	685	841	672
—CH—CH—	454	444	497
HC≡C<	583	—	—
—C≡C—	454	—	—
Cyclopentyl	—	1,380	1,300
Cyclohexyl	—	1,660	1,470
Phenyl	1,500	1,520	1,400
Phenylene	1,350	1,380	1,440
Naphthyl	2,340	—	—
—OH	—	754	462
—CO—	562	685	538
—CHO	—	—	599
—COO—	634	511	688
—COOH	—	651	998
—O—(C=O)—O—	—	767	904
—(C=O)—O—(C=O)−	—	767	1,160
—NH ₂	—	—	464
—NH—	—	—	368
—N<	—	—	125
—CHCN	896	1,120	901
—CN	839	982	725
—(C=O)−NH—	—	1,290	906
—O—(C=O)−NH—	—	1,480	1,040
—N=C=O	—	—	734
—H	164–205	140	—103
—S—	460	460	428
—SH	644	—	—
—F	250	164	84
—C1(primary)	552	471	420
—Br(primary)	695	614	528
—I	870	—	—
—CF ₂ —	307	—	—
—CF ₃	561	—	—
—O—N=O	900	—	—
—NO ₂	900	—	—
—PO ₄	1,020	—	—
—Si—	—77	—	—

^aAdapted from D. W. van Krevelen, Properties of Polymers, 3rd edition (Elsevier, Amsterdam), p. 200 (1990).

16.4 POLYMER-SOLVENT INTERACTION PARAMETER

The enthalpic component of polymer-solvent interaction parameter χ_H can be related to the solubility parameters via

$$\chi_H = \frac{V_i}{RT} (\delta_i - \delta_j)^2. \quad (16.28)$$

This equation links the polymer-solvent interaction parameter with the solubility parameters of polymer and solvent. For nonpolar systems the entropic term χ_s is usually taken to be a constant between 0.3 and 0.4 ($\chi_s = 0.34$ is often used) [41,122]. Equation (16.28) can thus be rewritten as

$$\chi = 0.34 + \frac{V_i}{RT} (\delta_i - \delta_j)^2 \quad (16.29)$$

for nonpolar systems $\chi = \chi_H + \chi_s$, where Eq. (16.27) is a good description of the enthalpic portion of the interaction parameter. According to Flory [123,124] a polymer *j* and a solvent *i* are expected to be completely miscible through the entire composition range provided that

$$\chi < \frac{1}{2} \left[1 + \left(\frac{V_i}{V_j} \right)^{1/2} \right]^2. \quad (16.30)$$

There is thus a critical polymer-solvent interaction parameter value

$$\chi_c = \frac{1}{2} \left[1 + \left(\frac{V_i}{V_j} \right)^{1/2} \right]^2 \quad (16.31)$$

and for $(V_i/V_j) \rightarrow 0$,

$$\chi_c = 0.5. \quad (16.32)$$

If χ must be less than 0.5 for full polymer-solvent miscibility, and χ_s is about 0.3, it follows that χ_H must be very small to meet the miscibility criterion, and that δ_i and δ_j must have very similar values. Specific interactions (such as hydrogen bonding between molecules of type *i* and type *j* to a greater extent than *i*-*i* and *j*-*j* hydrogen bonding) can result in the lower χ_H and thus enhance the mutual solubility.

For real polymer-solvent systems the experimental χ values and their dependences on composition, temperature, and molar mass provide useful indications of the nature and extent of the polymer-solvent interaction. For a polymer to be soluble in a solvent at a particular temperature, χ must be below 0.5 at high levels of ϕ_j . If the χ value is only slightly larger than 0.5, the polymer is expected to be swollen by the solvent.

There exist a number of extensive published collections of solubility parameters for both low-molecular-weight compounds (e.g., organic solvents) and high polymers [121,125–127]. Our purpose is to give a select number of solubility parameters data in Tables 16.2–16.5 that are representatives for the solvents used in various polymer technologies and the more important representative classes of high polymers used in industry and academic investigations. For the latter we have followed the suggested classes in Billmeyers's text [128]. We have taken some pains to include more recent data not necessarily found in the more exhaustive collections.

TABLE 16.2. Hildebrand parameters of representative solvents at 25 °C^a.

Solvent	$\delta[(MPa)^{1/2}]$	H-bonding tendency ^b
Acetaldehyde	21.1	m
Acetic acid	20.7	s
Acetic anhydride	21.1	s
Acetone	20.3	m
Acetonitrile	24.3	p
Acetophenone	21.7	m
Acetyl chloride	19.4	m
Acetylmorpholine (<i>N</i>)	23.7	m
Acetylpiridine (<i>N</i>)	22.9	s
Acetylpyrrolidine (<i>N</i>)	23.3	s
Acrolein	20.1	s
Acrylic acid	24.6	s
Acrylonitrile	21.5	p
Allyl acetate	18.8	m
Allyl alcohol	24.1	s
Allyl chloride	18.0	m
Ammonia	33.4	s
Amyl acetate (normal)	17.4	m
Amyl alcohol	20.5	s
Amylamine (normal)	17.8	s
Amyl bromide (normal)	15.6	m
Amyl chloride	17.0	m
Amylene	14.1	p
Amyl ether (normal, di-)	14.9	m
Amry formate (normal)	17.4	m
Amyl iodide (normal)	17.2	m
Anethole (<i>para</i>)	17.2	m
Aniline	21.1	s
Anthracene	20.3	p
Apcos#18 solvent	15.3	p
Apcos thinner	16.0	p
Aroclor 1248	18.0	p
Benzaldehyde	19.2	m
Benzene	18.8	p
Benzonitrile	17.2	p
Benzyl alcohol	24.8	s
Bicyclohexyl	17.4	p
Bromobenzene	20.3	p
Bromonaphthalene	21.7	p
Bromostyrene (<i>ortho</i>)	20.1	p
Butadiene-1,3	14.5	p
Butane (normal)	13.9	p
Butanediol-1,3	23.7	s
Butanediol-1,4	24.8	s
Butanediol-2,3	22.7	s
Butyl acetate (<i>iso</i>)	17.0	m
Butyl acetate (normal)	17.4	m
Butyl acylate (<i>iso</i>)	17.4	m
Butyl acylate (normal)	18.0	m
Butyl alcohol (<i>iso</i>)	21.5	s
Butyl alcohol (normal)	23.3	s
Butylamine (mono, normal)	17.8	s
Butyl bromide (normal)	17.8	m
Butyl (<i>iso</i>) butyrate (normal)	16.0	m

TABLE 16.2. Continued.

Solvent	$\delta[(MPa)^{1/2}]$	H-bonding tendency ^b
Butyl (normal) butyrate (normal)	16.6	m
Butyl chloride (<i>iso</i>)	16.6	m
Butylene-2,3 carbonate	24.8	m
Butylene (<i>iso</i>)	13.7	p
Butyl ether	16.0	m
Butyl formate (<i>iso</i>)	16.8	m
Butyl formate (normal)	18.2	m
Butyl idoide (normal)	17.6	m
Butyl lactate (normal)	19.2	m
Butyl methacrylate	16.8	m
Butyl stearate	15.3	m
Butyl propionate	18.0	m
Butyraldehyde	18.4	m
Butyric acid (<i>iso</i>)	21.1	s
Butyric acid (normal)	21.5	s
Butyrolactone	25.8	m
Butyronitrile (<i>iso</i>)	20.1	p
Butyronitrile (normal)	21.5	p
Caprolactam	26.0	m
Caprolactone	20.7	m
Capronitrile	19.2	p
Carbon disulfide	20.5	p
Carbon tetrachloride	17.6	p
Celanese solvent 601	18.8	m
Chloroacetonitrile	25.8	p
Chlorobenzene	19.4	p
Chloroethyl acetate (beta)	19.8	m
Chloroform	19.0	p
Chlorostyrene (<i>ortho</i> or <i>para</i>)	19.4	p
Chlorotoluene (<i>para</i>)	18.0	p
Cresol (<i>meta</i>)	20.9	s
Cyclobutanedione	22.5	m
Cyclohexane	16.8	p
Cyclohexanol	23.3	s
Cyclohexanone	20.3	m
Cyclopentane	17.8	p
Cyclopentanone	21.3	m
Cymene (<i>para</i>)	16.8	p
Decahydronaphthalene	18.0	p
Decane (normal)	13.5	p
Decyl acrylate (<i>iso</i>)	16.8	m
Diacetone alcohol	18.8	m
Diacetone alcohol methyl ether	16.8	m
Diacetylpirazine (<i>N,N</i>)	28.0	m
Diamyl phthalate	18.6	m
Dibenzyl ether	19.2	m
Dibromoethane-1,2	21.3	p
Dibromoethylene-1,2	20.7	p
Dibutoxyethyl phthalate (Kronisol)	16.4	m
Dibutylamine	16.6	s
Dibutyl fumarate	18.4	m
Dibutyl maleate	18.4	m
Dibutyl phenyl phosphate	17.8	m
Dibutyl phthalate	19.0	m

TABLE 16.2. *Continued.*

Solvent	$\delta[(MPa)^{1/2}]$	H-bonding tendency ^b
Dibutyl sebacate	18.8	m
Dichloroacetic acid	22.5	s
Dichlorobenzene (<i>ortho</i>)	20.5	p
Dichlorodifluoromethane (Freon 12)	11.3	p
Dichloroethyl ether	20.1	m
Dichloroethylene, <i>cis</i> -1,2	18.6	p
Dichloroethylene, <i>trans</i> -1,2	18.4	p
Dichlorofluoromethane (Freon 21)	17.0	p
Dichloropropane-1,2	18.4	p
Dichloropropane-2,2	16.8	p
Diethylacetamide (<i>N,N</i>)	20.3	m
Diethylamine	16.4	s
Diethyl carbonate	18.0	m
Diethylene glycol	24.8	s
Diethylene glycol monobutyl ether (normal)	19.4	m
Diethylene glycol monobutyl ether	20.9	m
Diethylene glycol monobutyl ether acetate	17.4	m
Diethylene glycol monolaurate	17.8	m
Diethyl ether	15.1	m
Diethylformamide (<i>N,N</i>)	21.7	m
Diethyl ketone	18.0	m
Diethyl maleate	20.3	m
Diethyl oxalate	17.6	m
Diethyl phthalate	20.5	m
Diethyl-2,2-propanediol-1,2 (heptylene glycol)	20.3	s
Diethyl sulfone	25.4	m
Difluoro-tetrachloroethane (Freon 112)	16.0	p
Diformylpiperazine (<i>N,N</i>)	31.5	m
Dihexyl ether	16.4	m
Epichlorohydrin	22.5	s
Ethane	12.3	p
Ethylacetamide (<i>N</i>)	25.2	s
Ethyl acetate	18.6	m
Ethyl acrylate	17.6	m
Ethyl alcohol	26.0	s
Ethylamine	20.5	s
Ethyl amyl ketone	16.8	m
Ethylbenzene	18.0	p
Ethyl benzoate	16.8	m
Ethyl bromide	19.6	m
Ethyl-2-butanol-1	21.5	s
Ethyl <i>n</i> -butyrate	17.4	m
Ethyl caprylate	14.9	m
Ethyl chloride	18.8	m
Ethyl cyanoacetate	22.5	m
Ethylene bromide	19.8	p
Ethylene carbonate	30.1	m
Ethylene chlorohydrin	25.0	s
Ethylene cyanohydrin	31.1	s
Ethylenediamine	25.2	s
Ethylene dichloride	20.1	p

TABLE 16.2. *Continued.*

Solvent	$\delta[(MPa)^{1/2}]$	H-bonding tendency ^b
Ethylene glycol	29.9	s
Ethylene glycol diacetate	20.5	m
Fluorocarbons, aliphatic	12.7	p
Fluorocarbons, aromatic	15.3	p
Formamide	39.3	s
Formic acid	24.8	s
Formylmorpholine (<i>N</i>)	26.6	m
Formylpiperidine (<i>N</i>)	23.5	m
Furane	19.2	m
Furfural	22.9	m
Furfuryl alcohol	25.6	s
Glycerol	33.8	s
Heptane (normal)	15.1	p
Heptyl alcohol (normal)	21.7	s
Hexamethylphosphoramide	21.5	s
Hexane (normal)	14.9	p
Hexanediaol-2,5	21.1	s
Hexene-1	15.1	p
Hexyl alcohol (normal)	21.9	s
Hydrazine	37.3	s
Hydrogen	6.9	p
Hydrogenated terphenyl	18.4	p
Hydrogen cyanide	24.8	s
Idobenzene	20.7	p
Isophorone	18.6	m
Isoprene	15.1	p
Lauryl alcohol	16.6	s
Low odor mineral spirits	14.1	p
Maleic anhydride	27.8	s
Malononitrile	30.9	p
Mesitylene	18.0	p
Mesityl oxide	18.4	m
Methacrylic acid	22.9	s
Methane	11.0	p
Methanol	29.7	s
Methylacetamide	29.9	s
Methyl acetate	19.6	m
Methyl acrylate	18.2	m
Methylamine	22.9	s
Methyl amyl acetate	16.4	m
Methyl amyl ketone	17.4	m
Methyl benzoate	21.5	m
Methyl bromide	19.6	m
Naphthalene	20.3	p
Neopentane	12.9	p
Neopentyl glycol	22.5	s
Nitrobenzene	20.5	p
Nitroethane	22.7	p
Nitromethane	26.0	p
Nitro- <i>n</i> -octane	14.3	p
Nitro-1-propane	21.1	p
Nitro-2-propane	20.3	p
Nonyl phenol	19.2	s
Octane (normal)	15.6	p
Octyl alcohol (normal)	21.1	s

TABLE 16.2. *Continued.*

Solvent	$\delta[(MPa)^{1/2}]$	H-bonding tendency ^b
Pentachloroethane	19.2	p
Pentane (normal)	14.3	p
Pentanediol-1,5	23.5	s
Pentanediol-2,4	22.1	s
Perchloroethylene	19.0	p
Perfluoroheptane	11.9	p
Perfluoromethylcyclohexane	12.3	p
Phenathrene	20.1	p
Phenylhydrazine	25.6	s
Pine oil	17.6	p
Piperidine	17.8	s
Piperidone	27.8	s
Propane	13.1	p
Propyl formate	18.8	m
Pyridine	21.9	s
Quinoline	22.1	s
Styrene	19.0	p
Styrene oxide	21.5	m
Succinic anhydride	31.5	s
Tetrachloroethane-1,1,2,2	19.8	p
Tetrachloroethylene	19.0	p
Tetraethylene glycol	20.3	s
Tetrahydrofuran	18.6	m
Tetrahydronaphthalene	19.4	p
Tetramethylene sulfone	27.4	m
Tetramethyloxamide	23.3	m
Thiophene	20.1	m
Toluene	18.2	p

TABLE 16.2. *Continued.*

Solvent	$\delta[(MPa)^{1/2}]$	H-bonding tendency ^b
Tolylenediiisocyanate	23.7	s
Tributylamine	15.8	s
Trichloroethane-1,1,2	19.6	p
Trichloroethylene	18.8	p
Trichlorofluoromethane	15.5	p
Trichlorotrifluoroethane	14.9	p
Tricresyl phosphate	17.2	m
Triethylamine	15.1	s
Triethyleneglycol	21.9	s
Triethylenetetramine	22.7	s
Trimethyl-3,5,5-hexanol	17.2	s
Triphenyl phosphate	17.6	m
Triphenyl phosphite	19.0	m
Tripropylene glycol	18.8	s
Turpentine	16.6	p
Valeric acid (normal)	20.1	s
Valeronitrile (normal)	15.6	p
Varnolene (varsol #2)	19.6	p
Vinyel acetate	18.4	m
Vinyel chloride	16.0	m
Vinyel toluene	18.6	p
V M & P naphtha	15.6	p
Water	47.9	s
Xylene	18.0	p

^aAdapted from J. Brandrup, E. H. Immergut, and E. A. Grulke, *Polymer Handbook*, 4th edition, John Wiley & Sons, New York (1999).

^bp denotes poor; m, moderate; s, strong.

TABLE 16.3. Hansen solubility parameters of representative liquids at 25 °C^a.

Solvent	$V(\text{cm}^3/\text{mol})$	Solubility parameter $[(MPa)^{1/2}]$			
		δ_d	δ_p	δ_h	δ_t
Acetaldehyde	57.1	14.7	8.0	11.3	20.3
Acetic acid	57.1	14.5	8.0	13.5	21.3
Acetic anhydride	94.5	16.0	11.7	10.2	22.3
Acetone	74.0	15.5	10.4	7.0	20.1
Acetonitrile	52.6	15.3	18.0	6.1	24.6
Acetophenone	117.4	19.6	8.6	3.7	21.7
Acetyl chloride	71.0	15.8	10.6	3.9	19.4
Acrylonitrile	67.1	16.4	17.4	6.8	24.8
Allyl alcohol	68.4	16.2	10.8	16.8	25.8
Amyl (i) acetate	148.8	15.3	3.1	7.0	17.2
Aniline	91.5	19.4	5.1	10.2	22.5
Anisole	119.1	17.8	4.1	6.8	19.4
Benzaldehyde	101.5	19.4	7.4	5.3	21.5
Benzene	89.4	18.4	0.0	2.0	18.6
Benzenediol-1,3	87.5	18.0	8.4	21.1	28.8
Benzoic acid	100.0	18.2	7.0	9.8	21.9
Benzonitrile	102.6	17.4	9.0	3.3	19.8
Benzyl alcohol	103.6	18.4	6.3	13.7	23.7

TABLE 16.3. *Continued.*

Solvent	<i>V</i> (cm ³ /mol)	Solubility parameter [(MPa) ^{1/2}]			
		δ_d	δ_p	δ_h	δ_t
Biphenyl	154.1	21.5	1.0	2.0	21.7
Bis(2-chloroethyl) ether	117.6	18.8	9.0	5.7	21.7
Bis-(<i>m</i> -phenoxyphenyl) ether	373.0	19.6	3.1	5.1	20.5
Bromobenzene	105.3	20.5	5.5	4.1	21.7
Bromochloromethane	65.0	17.4	5.7	3.5	18.6
Bromoform	87.5	21.5	4.1	6.1	22.7
Bromotrifluoromethane	97.0	9.6	2.5	0.0	10.0
Butanol-1	91.5	16.0	5.7	15.8	23.1
Butanol-2	92.0	15.8	5.7	14.5	22.1
Butyl (<i>i</i>) acetate	133.5	15.1	3.7	6.3	16.8
Butyl (<i>n</i>) acetate	132.5	15.8	3.7	6.3	17.4
Butyl (<i>n</i>) benzyl phthalate	306.0	19.0	11.3	3.1	22.3
Butylamine- <i>n</i>	99.0	16.2	4.5	8.0	18.6
Butylchloride (<i>n</i>)	104.9	16.4	5.5	2.0	17.4
Butyl- <i>n</i> lactate	149.0	15.8	6.5	10.2	19.8
Butyraldehyde	88.5	14.7	5.3	7.0	17.2
Butyric- <i>n</i> acid	110.0	14.9	4.1	10.6	18.8
Butyronitrile	87.0	15.3	12.5	5.1	20.5
Carbon disulfide	60.0	20.5	0.0	0.6	20.5
Carbon tetrachloride	97.1	17.8	0.0	0.6	17.8
Chloro-3-propanol	84.2	17.6	5.7	14.7	23.7
Chlorobenzene	102.1	19.0	4.3	2.0	19.6
Chlorodifluoromethane	72.9	12.3	6.3	5.7	14.9
Chloroform	80.7	17.8	3.1	5.7	19.0
Cyclohexanol	106.0	17.4	4.1	13.5	22.5
Cyclohexanone	104.0	17.8	6.3	5.1	19.6
Cyclohexylamine	115.2	17.4	3.1	6.5	18.8
Decanol-1	191.8	17.6	2.7	10.0	20.5
Di-(2-chloro- <i>t</i> -propyl) ether	146.0	19.0	8.2	5.1	21.3
Di-(2-methoxyethyl) ether	142.0	15.8	6.1	9.2	19.2
Di-(<i>t</i> -butyl) ketone	177.1	16.0	3.7	4.1	16.8
Diacetone alcohol	124.2	15.8	8.2	10.8	20.9
Dibenzyl ether	192.7	17.4	3.7	7.4	19.2
Di-butyl stearate	382.0	14.5	3.7	3.5	15.3
Dichlorobenzene (o)	112.8	19.2	6.3	3.3	20.5
Dichloroethane-1,1	84.8	16.6	8.2	0.4	18.4
Dichloroethylene-1,1	79.0	17.0	6.8	4.5	18.8
Dichlorofluoromethane	75.4	15.8	3.1	5.7	17.0
Dichlorofluoromethane	92.3	12.3	2.0	0.0	12.5
Diethyl carbonate	121.0	16.6	3.1	6.1	18.0
Diethyl ether	104.8	14.5	2.9	5.1	15.8
Diethyl ketone	106.4	15.8	7.6	4.7	18.2
Diethyl phthalate	198.0	17.6	9.6	4.5	20.5
Diethyl sulfate	131.5	15.8	14.7	7.2	22.7
Diethyl sulfide	108.2	17.0	3.1	2.0	17.4
Diethylamine	103.2	14.9	2.3	6.1	16.4
Diethylbenzene (<i>p</i>)	156.9	18.0	0.0	0.6	18.0
Diethylene glycol monobutyl- <i>n</i> ether	170.6	16.0	7.0	10.6	20.5
Diethylene glycol monoethyl ether	130.9	16.2	9.2	12.3	22.3
Diethylene glycol monomethyl ether	118.0	16.2	7.8	12.7	21.9
Diethylenetriamine	108.0	16.8	13.3	14.3	25.8
Dimethyl phthalate	163.0	18.6	10.8	4.9	22.1
Dimethyl sulfone	75.0	19.0	19.4	12.3	29.9

TABLE 16.3. *Continued.*

Solvent	V (cm ³ /mol)	Solubility parameter [(MPa) ^{1/2}]			
		δ_d	δ_p	δ_h	δ_t
Dimethyl sulfoxide	71.3	18.4	16.4	10.2	26.6
Dimethyl-1,3-butanol-1	127.2	15.3	3.3	12.3	19.8
Dimethylformamide	77.0	17.4	13.7	11.3	24.8
Dimethylformamide- <i>N,N</i>	92.5	16.8	11.5	10.2	22.7
Dimethylhydrazine-1,1	76.0	15.3	5.9	11.0	19.8
Di- <i>n</i> -butyl phthalate	266.0	17.8	8.6	4.1	20.3
Di- <i>n</i> -butyl sebacate	339.0	13.9	4.5	4.1	16.2
Di- <i>n</i> -propylamine	136.9	15.3	1.4	4.1	16.0
Diocetyl phthalate	277.0	16.6	7.0	3.1	18.2
Dioxane-1,4	85.7	19.0	1.8	7.4	20.5
Epichlorhydrin	79.9	19.0	10.2	3.7	21.9
Ethanethiol	74.3	15.8	6.5	7.2	18.4
Ethanolamine	60.2	17.2	15.5	21.3	31.5
Ethanolamine	58.5	15.8	8.8	19.4	26.6
Ethoxyethyl acetate-2	136.2	16.0	4.7	10.6	19.6
Ethyl acetate	98.5	15.8	5.3	7.2	18.2
Ethyl bromide	76.9	16.6	8.0	5.1	19.0
Ethyl chloroformate	95.6	15.5	10.0	6.8	19.6
Ethyl cinnamate	166.8	18.4	8.2	4.1	20.5
Ethyl formate	80.2	15.5	8.4	8.4	19.6
Ethyl lactate	115.0	16.0	7.6	12.5	21.7
Ethyl-1-butanol-1	123.2	15.8	4.3	13.5	21.3
Ethyl-2-hexanol-1	157.0	16.0	3.3	11.9	20.1
Ethylbenzene	123.1	17.8	0.6	1.4	17.8
Ethylene carbonate	66.0	19.4	21.7	5.1	29.5
Ethylene cyanohydrin	68.3	17.2	18.8	17.6	30.9
Ethylene diamine	67.3	16.6	8.8	17.0	25.4
Ethylene dibromide	87.0	19.6	6.8	12.1	23.9
Ethylene dichloride	79.4	19.0	7.4	4.1	20.9
Ethylene glycol monobutyl- <i>n</i> ether	131.6	16.0	5.1	12.3	20.9
Ethylene glycol monoethyl ether	97.8	16.2	9.2	14.3	23.5
Ethylene glycol monomethyl ether	79.1	16.2	9.2	16.4	24.8
Formamide	39.8	17.2	26.2	19.0	36.6
Formic acid	37.8	14.3	11.9	16.6	25.0
Furan	72.5	17.8	1.8	5.3	18.6
Furfuraldehyde	83.2	18.6	14.9	5.1	24.3
Furfuryl alcohol	86.5	17.4	7.6	15.1	24.3
Hexamethyl phosphoramide	175.7	18.4	8.6	11.3	23.3
Isophorone	150.5	16.6	8.2	7.4	19.8
Mesityl oxide	115.6	16.4	7.2	6.1	18.8
Mesitylene	139.8	18.0	0.0	0.6	18.0
Methanol	40.7	15.1	12.3	22.3	29.7
Methyl acetate	79.7	15.5	7.2	7.6	18.8
Methyl chloride	55.4	15.3	6.1	3.9	17.0
Methyl ethyl ketone	90.1	16.0	9.0	5.1	19.0
Methyl <i>i</i> -amyl ketone	142.8	16.0	5.7	4.1	17.4
Methyl <i>i</i> -butyl ketone	125.8	15.3	6.1	4.1	17.0
Methyl oleate	340.0	14.5	3.9	3.7	15.5
Methyl-2-propanol-1	92.8	15.1	5.7	16.0	22.7
Methylene dichloride	63.9	18.2	6.3	6.1	20.3
Methylene diiodide	80.5	17.8	3.9	5.5	19.0
Methylnaphthalene-1	138.8	20.6	0.8	4.7	21.2
Methyl- <i>N</i> -pyrrolidone-2	96.5	18.0	12.3	7.2	22.9

TABLE 16.3. *Continued.*

Solvent	V (cm ³ /mol)	Solubility parameter [(MPa) ^{1/2}]			
		δ_d	δ_p	δ_h	δ_t
Morpholine	87.1	18.8	4.9	9.2	21.5
Naphthalene	111.5	19.2	2.0	5.9	20.0
Nitrobenzene	102.7	20.1	8.6	4.1	22.1
Nitroethane	71.5	16.0	15.5	4.5	22.7
Nitromethane	54.3	15.8	18.8	5.1	25.0
Nitropropane-2	86.9	16.2	12.1	4.1	20.7
Nonyl phenoxy ethanol	275.0	16.8	10.2	8.4	21.3
Octanol-1	157.7	17.0	3.3	11.9	20.9
Octanol-2	159.1	16.2	4.9	11.0	20.3
Octoic- <i>n</i> acid	159.0	15.1	3.3	8.2	17.6
Oleic acid	320.0	14.3	3.1	5.5	15.8
Oleyl alcohol	316.0	14.3	2.7	8.0	16.6
Pentanol-1	109.0	16.0	4.5	13.9	21.7
Perfluorodimethylcyclohexane	217.4	12.5	0.0	0.0	12.5
Perfluoromethylcyclohexane	196.0	12.5	0.0	0.0	12.5
Perfluoro- <i>n</i> -heptane	227.3	12.1	0.0	0.0	12.1
Phenol	87.5	18.0	5.9	14.9	24.1
Propanol-1	75.2	16.0	6.8	17.4	24.6
Propanol-2	76.8	15.8	6.1	16.4	23.5
Propionitrile	70.9	15.3	14.3	5.5	21.7
Propyl (<i>i</i>) palmitate	330.0	14.3	3.9	3.7	15.3
Propyl (<i>n</i>) chloride	88.1	16.0	7.8	2.0	17.8
Propylamine- <i>n</i>	83.0	17.0	4.9	8.6	19.6
Propylene carbonate	85.0	20.1	18.0	4.1	27.2
Pyridine	80.9	19.0	8.8	5.9	21.7
Pyrrolidone-2	76.0	19.4	17.4	11.3	28.4
Quinoline	118.0	19.4	7.0	7.6	22.1
Stearic acid	326.0	16.4	3.3	5.5	17.6
Styrene	115.6	18.6	1.0	4.1	19.0
Succinic anhydride	66.8	18.6	19.2	16.6	31.5
Tetrachloroethane-1,1,2,2	105.2	18.8	5.1	9.4	21.7
Tetrachloroethylene	101.1	19.0	6.5	2.9	20.3
Tetrahydrofuran	81.7	16.8	5.7	8.0	19.4
Tetrahydronaphthalene	136.0	19.6	2.0	2.9	20.0
Tetramethylurea	120.4	16.8	8.2	11.0	21.7
Toluene	106.8	18.0	1.4	2.0	18.2
Trichlorobiphenyl	187.0	19.2	5.3	4.1	20.5
Trichloroethane-1,1,1	100.4	17.0	4.3	2.0	17.6
Trichloroethylene	90.2	18.0	3.1	5.3	19.0
Trichlorofluoromethane	92.8	15.3	2.0	0.0	15.5
Tricresyl phosphate	613.0	19.0	12.3	4.5	23.1
Tridecyl alcohol	242.0	14.3	3.1	9.0	17.2
Triethyl phosphate	171.0	16.8	11.5	9.2	22.3
Triethylene glycol mono-oleyl ether	418.5	13.3	3.1	8.4	16.0
Trimethyl phosphate	99.9	16.8	16.0	10.2	25.4
Tri- <i>n</i> -butyl phosphate	345.0	16.4	6.3	4.3	18.0
Water	18.0	15.5	16.0	42.4	47.9
Xylene (<i>o</i>)	121.2	17.8	1.0	3.1	18.0

^aAdapted from J. Brandrup, E. H. Immergut, and E. A. Grulke, *Polymer Handbook*, 4th edition, John Wiley & Sons, New York (1999).

TABLE 16.4. Solubility parameters of representative polymers.

Polymer	$\delta(\text{MPa}^{1/2})$	T (°C)	Method	Reference
Cellulose	32.02			[129]
Cellulose diacetate	23.22		Calc.	[39]
Cellulose nitrate (11.83% N)	21.44		Calc.	[39]
Epoxy resin	22.3			[130]
Natural rubber	16.2			[131]
	17.09			[132]
Poly(4-acetoxy styrene)	22.7	25	Visc.	[133]
Poly(acrylic acid)				
—, butyl ester	18.0	35		[134]
	18.52		Swelling	[134]
—, methyl ester	20.77		Swelling	[134]
	20.7		Swelling	[135]
Poly(acrylonitrile)	26.09	25	Calc.	[39]
Poly(butadiene)	16.2	75	IPGC	[136]
	17.15		Calc.	[39]
Poly(butadiene-co-acrylonitrile)				
BUNA N (72/25)	18.93	25	Calc.	[39]
(61/39)	20.5	75	IPGC	[136]
Poly(butadiene-co-styrene)				
BUNA S (85/15)	17.41		Calc.	[137]
	17.39		Obs.	[137]
Poly(butadiene-co-vinylpyridine)				
(72/25)	19.13			[132]
Poly(chloroprene)	18.42	25		[129]
	19.19		Calc.	[39]
	17.6		Swelling	[131]
Poly(dimethyl siloxane)	14.9	30	Calc.	[138]
Poly(ethylene)	16.6		Calc.	[39]
Poly(ethylene)	16.4		Calc.	[139]
	16.2		Obs.	[140]
Poly(ethylene-co-vinyl-acetate)	18.6	25	IPGC	[93]
	17.0	75	IPGC	[136]
Poly(tetra-fluoroethylene)	12.7		Calc.	[39]
Poly(heptamethylene <i>p,p'</i> -bibenzoate)	19.50	25	Visc.	[141]
Poly(4-hydroxystyrene)	23.9	25	Visc.	[133]
Poly(isobutene)	16.06	35	Av.	[142]
	16.47		Swelling	[142]
	16.06	25		[129]
Poly(isobutene-co-isoprene) butyl rubber	16.47			[122]
Poly(isoprene)	15.18	25	Calc.	[112]
1,4- <i>cis</i>	16.68	25		[142]
	16.57	35		[142]
	20.46	35	Swelling	[142]
	16.6		Swelling	[134]
	16.68	25	Calc.	[39]
Poly(methacrylic acid)				
—, isobutyl ester	14.7	140	IPGC	[91]
—, ethyl ester	18.31		Swelling	[135]
—, methyl ester	18.58	25		[87]
Poly(methacrylonitrile)	21.9		Calc.	[39]
Poly(methylene)	14.3	20	Extrap.	[143]
Poly(α -methyl styrene)	18.75	30	Visc.	[144]
Poly(σ -methylstyrene-co-acrylonitrile)	16.4	180	IPGC	[145]
Poly(oxyethylene)	20.2	25	IPGC	[91]
Poly(propylene)	18.8	25		[114]
Poly(styrene)	18.72	35		[142]
Poly(styrene-co- <i>n</i> -butyl-methacrylate)	15.1	140	IPGC	[91]
Poly(thioethylene)	19.19		Swelling	[131]

TABLE 16.4. *Continued.*

Polymer	$\delta(\text{MPa}^{1/2})$	T (°C)	Method	Reference
Poly(vinyl acetate)	19.62	25	Calc.	[112]
Poly(vinyl alcohol)	25.78			[129]
Poly(vinyl chloride)	19.28		Calc.	[112]
	19.8		Obs.	[94]
Poly(vinyl chloride), chlorinated	19.0	25	Visc.	[146]
Poly(vinyl propionate)	18.01	35		[147]

TABLE 16.5. *Hansen solubility parameters of representative polymers.*

Polymer (trade name, supplier)	Solubility parameter (MPa ^{1/2})				Reference
	δ_d	δ_p	δ_h	δ_t	
Acrylonitrile-butadiene elastomer (Hycar 1052, BF Goodrich)	18.6	8.8	4.2	21.0	[54]
Alcohol soluble resin (Pentalyn 255, Hercules)	17.5	9.3	14.3	24.4	[54]
Alcohol soluble resin (Pentalyn 830, Hercules)	20.5	5.8	10.9	23.5	[54]
Alkyd, long oil (66% oil length, Plexal P65, Polyplex)	20.42	3.44	4.56	21.20	[54]
Alkyd, short oil (Coconut oil 34% phthalic anhydride; Plexal C34)	18.50	9.21	4.91	21.24	[54]
Blocked isocyanate (Phenol, Suprasec F5100, ICI)	20.19	13.16	13.07	27.42	[54]
Cellulose acetate (Cellidore A, Bayer)	18.60	12.73	11.01	25.08	[54]
Cellulose nitrate (1/2 s; H-23, Hagedon)	15.41	14.73	8.84	23.08	[54]
Epoxy (Epikote 1001, Shell)	20.36	12.03	11.48	26.29	[54]
Ester gum (Ester gum BL, Hercules)	19.64	4.73	7.77	21.65	[54]
Furfuryl alcohol resin (Durez 14383, Hooker Chemical)	21.16	13.56	12.81	28.21	[54]
Hexamethoxymethyl melamine (Cymel 300 American Cyanimid)	20.36	8.53	10.64	24.51	[54]
Isoprene elastomer (Cariflex IR 305, Shell)	16.57	1.41	-0.82	16.65	[54]
Methacrylonitrile/methacrylic acid copolymer	17.39	14.32	12.28	25.78	[148]
Nylon 66	18.62	5.11	12.28	22.87	[6]
Nylon 66 (Zytel, DuPont)	18.62	0.00	14.12	23.37	[54]
Petroleum hydrocarbon resin (Piceopale 110, Penn. Ind. Chem.)	17.55	11.19	3.60	17.96	[54]
Phenolic resin (Resole, Phenodur 373 U Chemische Werke Albert)	19.74	11.62	14.59	27.15	[54]
Phenolic resin, pure (Super Beckacite 1001, Reichhold)	23.26	6.55	8.35	25.57	[54]
Poly(4-acetoxy, α -acetoxy styrene)	17.80	10.23	7.37	21.89	[149]
Poly(4-acetoxy styrene)	17.80	9.00	8.39	21.69	[133]
Poly(acrylonitrile)	18.21	16.16	6.75	25.27	[6]
Polyamid, thermoplastic (Versamid 930, General Mills)	17.43	-1.92	14.89	23.02	[54]
Poly(<i>p</i> -benzamide)	18.0	11.9	7.9	23.0	[150]
cis-Poly(butadiene)elastomer (Bunahuls CB10, Chemische Werke Huels)	17.53	2.25	3.42	18.00	[54]
Poly(isobutylene) (Lutonal IC/123, BASF)	14.53	2.52	4.66	15.47	[54]
Poly(ethyl methacrylate) (Lucite 2042, DuPont)	17.60	9.66	3.97	20.46	[54]
Poly(ethylene terephthalate)	19.44	3.48	8.59	21.54	[6]
Poly(4-hydroxystyrene)	17.60	10.03	13.71	24.55	[133]
Poly(methacrylic acid)	17.39	12.48	15.96	26.80	[148]
Poly(methacrylonitrile)	18.00	15.96	7.98	25.37	[148]
Poly(methyl methacrylate)					
Poly(sulfone), Bisphenol A (Polystyrene LG, BASF)	21.28	5.75	4.30	22.47	[54]
Poly(sulfone), Bisphenol A (Udel)	19.03	0.00	6.96	20.26	[151]
Poly(vinyl acetate) (Mowilith 50, Hoechst)	20.93	11.27	9.66	25.66	[54]
Poly(vinyl butyral) (Butvar B76, Shawinigan)	18.60	4.36	13.03	23.12	[54]
Poly(vinyl chloride) (Vipla KR K = 50, Montecatini)	18.23	7.53	8.35	21.42	[54]
Poly(vinyl chloride)	18.72	10.03	3.07	21.46	[113]
Poly(vinyl chloride)	18.82	10.03	3.07	21.54	[6]
Saturated polyester (Desmophen 850, Bayer)	21.54	14.94	12.28	28.95	[54]

TABLE 16.5. *Continued.*

Polymer (trade name, supplier)	Solubility parameter (MPa ^{1/2})				Reference
	δ_d	δ_p	δ_h	δ_t	
Styrene-butadiene (SBR) raw elastomer (Polysar 5630, Polymer Corp.)	17.55	3.36	2.70	18.07	[54]
Terpene resin (Piccolyte S-1000, Penn. Ind. Chem.)	16.47	0.37	2.84	16.72	[54]
Urea-formaldehyde resin (Plastopal H, BASF)	20.81	8.29	12.71	25.74	[54]
Vinylidene cyanide/4-acetoxy, α -acetoxy styrene copolymer	21.48	11.25	7.16	21.89	[149]
Vinylidene cyanide/4-chloro-styrene copolymer (Rohm and Haas)	16.98	12.07	8.18	22.38	[149]
Poly(styrene)	18.64	10.52	7.51	22.69	[54]

ACKNOWLEDGMENT

The preparation of this chapter was supported by the National Science Foundation Grant No. DMR 9023541.

REFERENCES

- R. F. Blanks, Polym. Plast. Technol. Eng. **8** (1), 13 (1977).
- M. T. Shaw, J. Appl. Polym. Sci. **18**, 449 (1974).
- S. Piccarolo and G. Titomanilo, Ind. Eng. Chem. Proc. Des. Dev. **22**, 146 (1982).
- B. Schneier, Polym. Lett. **10**, 245 (1972).
- P. E. Froehling and L. T. Hillegers, Polymer **22**, 261 (1981).
- Z. Rigbi, Polymer **19**, 1229 (1978).
- Shell Chemicals, *Solubility Parameters*, 2nd ed., Tech. Bull. International Chemical Society (X)/78/1 (1978).
- Shell Chemicals, *Solvent Systems Design*, Tech. Bull. International Chemical Society (X)/78/2 (1987).
- J. Polak, Collect. Czech. Chem. Commun. **31**, 1483 (1966).
- J. H. Hildebrand and R. L. Scott, *Solubility of Non-Electrolytes*, 3rd ed. (Reinhold, New York, 1950; Dover, New York, 1964).
- J. H. Hildebrand and R. L. Scott, *Regular Solutions* (Prentice-Hall, Englewood Cliffs, NJ, 1962).
- J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, *Regular and Related Solutions* (Van Nostrand-Reinhold, Princeton, NJ, 1970).
- E. Bagley *et al.*, J. Paint Technol. **41**, 495 (1969).
- E. B. Bagley, T. P. Nelson, J. W. Barlow, and S. A. Chen, Ind. Eng. Chem. Fund. **9**, 93 (1970).
- E. Bagley *et al.*, J. Paint Technol. **43**, 35 (1971).
- J. D. van der Waals, Z. Phys. Chem. **5**, 133 (1890).
- J. J. van Laar, *Sechs Vorträge über das Thermodynamische Potential* (Vieweg, Braunschweig, 1906).
- G. Scatchard, Chem. Rev. **8**, 321 (1931).
- G. Scatchard, Chem. Rev. **44**, 7 (1949).
- J. H. Hildebrand, J. Am. Chem. Soc. **38**, 1452 (1916).
- J. H. Hildebrand, J. Am. Chem. Soc. **41**, 1067 (1919).
- J. H. Hildebrand, Phys. Rev. **34**, 649 (1929).
- J. H. Hildebrand, J. Am. Chem. Soc. **51**, 66 (1929).
- J. H. Hildebrand, *Solubility of Non-Electrolytes*, 2nd ed. (Reinhold, New York, 1936; Russian translation: GONTI, Moscow, 1938).
- J. H. Hildebrand, Chem. Rev. **44**, 37 (1949).
- J. H. Hildebrand, Nature (London) **168**, 868 (1951).
- J. H. Hildebrand, J. Phys. Chem. **58**, 671 (1954).
- J. H. Hildebrand, Science **150**, 441 (1965).
- J. H. Hildebrand, in *Structure-Solubility Relationships in Polymers*, Proceedings of the Symposium, 1976, edited by F. W. Harris and R. W. Seymour, (Academic, New York, 1977), p. 1.
- J. H. Hildebrand, Ind. Eng. Chem. Fundam. **17**, 365 (1978).
- J. H. Hildebrand, Proc. Natl. Acad. Sci. USA **76**, 6040 (1979).
- J. H. Hildebrand and J. H. Dymond, Proc. Natl. Acad. Sci. USA **54**, 1001 (1965).
- J. H. Hildebrand and R. H. Lamoreaux, Ind. Eng. Chem. Fundam. **13**, 110 (1974).
- R. L. Scott, thesis, Princeton University, Princeton, NJ, 1945.
- R. L. Scott, J. Am. Chem. Soc. **70**, 4090 (1948).
- R. L. Scott, Disc. Faraday Soc. **15**, 44 (1953).
- A. J. Staverman, Rec. Trav. Chim. Pays-Bas **60**, 827 (1941).
- A. E. van Arkel, Trans. Faraday Soc. **42B**, 81 (1946).
- P. A. Small, J. Appl. Chem. **3**, 71 (1953).
- R. Andersen, Ph.D. thesis, Dept. of Chemical Engineering, University of California, Berkeley, 1961.
- R. F. Blanks and J. M. Prausnitz, Ind. Eng. Chem. Fundam. **3**, 1 (1964).
- R. Kumar and J. M. Prausnitz, in *Solutions and Solubilities*, edited by M. R. J. Dack (Wiley-Interscience, New York, 1975), Part 1, Chap. 5.
- J. M. Prausnitz and R. Anderson, Am. Inst. Chem. Eng. J. **7**, 96 (1961).
- R. F. Weimer and J. M. Prausnitz, Hydrocarbon Proc. Petr. Ref. **44**, 237 (1965).
- J. M. Prausnitz and F. H. Shair, Am. Inst. Chem. Eng. J. **7**, 682 (1961).
- H. G. Harris and J. M. Prausnitz, Ind. Eng. Chem. Fund. **8**, 180 (1969).
- C. M. Hansen, Doctoral dissertation (Danish Technical Press, Copenhagen, 1967).
- C. M. Hansen, J. Paint Technol. **39**, 104 (1967).
- C. M. Hansen, J. Paint Technol. **39**, 505 (1967).
- C. M. Hansen, Skand. Tidskr. Färg Lack **13**, 132 (1967).
- C. M. Hansen, Skand. Tidskr. Färg Lack **14** (2), 28 (1968).
- C. M. Hansen, Ind. Eng. Chem. Prod. Res. Dev. **8**, 2 (1969).
- C. M. Hansen, J. Paint Technol. **42**, 660 (1970).
- C. M. Hansen, Skand. Tidskr. Färg Lack **17**, 69 (1971).
- C. M. Hansen, J. Paint Technol. **44**, 57 (1972).
- C. M. Hansen, Chemtech **2**, 547 (1972).
- C. M. Hansen, in *Solvents Theory and Practice*, Advances in Chemistry Series No. 124, edited by R. W. Tess (American Chemical Society, Washington, D.C., 1973), Chap. 4.
- C. M. Hansen, Ind. Eng. Chem. Prod. Res. Dev. **16**, 266 (1977).
- C. M. Hansen, Farbe Lack **83**, 595 (1977).
- C. M. Hansen, Fed. Assoc. Tech. Ind. Peint. Vernis Emaux Encres Impr. Eur. Cont. Congr. **14**, 97 (1978).
- C. M. Hansen, in *Macromolecular Solutions: Solvent-Polarity Relationships in Polymers*, Proceedings of the Symposium, American Chemical Society, New York, 1981, edited by R. B. Seymour and G. A. Stahl (Pergamon, New York, 1982), p. 1; Org. Coat. Plast. Chem. **45**, 227 (1981).
- C. M. Hansen, Prog. Org. Coat. **10**, 331 (1982).
- C. M. Hansen and A. Beerbower, in *The Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed., edited by A. Standen (Interscience, New York, 1971), Suppl. Vol. p. 889.
- C. M. Hansen and P. E. Pierce, Ind. Eng. Chem. Prod. Res. Dev. **13**, 218 (1974).
- K. Skaarup, Skand. Tidskr. Färg Lack **14**, 45 (1968).
- C. M. Hansen and K. Skaarup, J. Paint Technol. **39**, 511 (1967).
- C. M. Hansen and K. Skaarup, Dan. Kemi **48**, 81 (1967).
- C. M. Hansen and E. Wallström, J. Adhesion **15**, 275 (1983).
- E. M. Arnett, Progr. Phys. Org. Chem. **1**, 223 (1963).
- W. Gerrard, A. M. A. Mineer, and P. L. Wyvill, J. Appl. Chem. **10**, 115 (1960).
- W. Gerrard, *Solubility of Gases and Liquids: A Graphic Approach* (Plenum, New York, 1976).

72. M. R. J. Dack, in *Solutions and Solubilities*, edited by M. R. J. Dack (Wiley-Interscience, New York, 1976), Part II, Chap. 11.
73. V. Gutmann, Rec. Chem. Progr. **30**, 169 (1969).
74. V. Gutmann, Z. Chem. **20**, 37 (1980).
75. J. Amoros, J. R. Solana, and E. Villar, Mater. Chem. Phys. **10**, 557 (1984).
76. R. F. Fedors, Jet Propul. Lab. Quart. Tech. Rev. **3**, 45 (1973); Polym. Eng. Sci. **14**, 147, (1974); **14**, 472 (1974).
77. K. M. Watson, Ind. Eng. Chem. **23**, 360 (1931); **35**, 398 (1943).
78. A. S. Michaels, ASTM Tech. Pub. **340**, 3 (1963).
79. D. M. Koenen and C. A. Smolders, J. Appl. Polym. Sci. **19**, 1163 (1975).
80. I. A. Wiehe and E. B. Bagley, Am. Inst. Chem. Eng. J. **13**, 836 (1967).
81. E. B. Bagley and S.-A. Chen, J. Paint Technol. **41**, 494 (1969).
82. J. M. Scigiano, Ph.D. thesis, Washington University, St. Louis, MO, 1972; Diss. Abstr. B **32**, 6984 (1972).
83. I. Vavruch (personal communication).
84. J. H. Sewell, RAE Technical Report No. 66185, June, 1966.
85. A. Beerbower and J. R. Dickey, Am. Soc. Lubr. Eng. Trans. **12**, 1 (1969).
86. O. Olabisi and R. Simha, J. Appl. Polym. Sci. **21**, 149 (1977).
87. G. M. Bristow and W. F. Watson, Trans. Faraday Soc. **54**, 1731 (1958); **54**, 1742 (1958).
88. P. Alessi, I. Kikic, G. Torriano, and A. Papo, J. Coatings Technol. **51**, 62 (1979).
89. G. DiPaola-Baranayi and J. E. Guillet, Macromolecules **11**, 228 (1978).
90. G. DiPaola-Baranayi, J. E. Guillet, J. Klein, and H.-E. Jeberein, J. Chromatogr. **166**, 349 (1978).
91. G. DiPaola-Baranayi, Macromolecules **15**, 622 (1982).
92. K. Ito and J. E. Guillet, Macromolecules **12**, 1163 (1979).
93. J. E. G. Lipson and J. E. Guillet, J. Coatings Technol. **54**, 90 (1982).
94. M. Magat, J. Chem. Phys. **46**, 344 (1949).
95. D. Patterson, Macromolecules **4**, 30 (1971).
96. D. Patterson, Y. B. Tewari, H. P. Schreiber, and J. E. Guillet, Macromolecules **4**, 356 (1971).
97. C. Smidsrod and J. E. Guillet, Macromolecules **2**, 272 (1968).
98. W. A. Ruff, C. J. Glover, and A. T. Watson, Am. Inst. Chem. Eng. J. **32**, 1948 (1986).
99. W. A. Ruff, C. J. Glover, A. T. Watson, W. R. Lau, and J. C. Holste, Am. Inst. Chem. Eng. J. **32**, 1954 (1986).
100. S. Wu, J. Phys. Chem. **27**, 3332 (1968).
101. P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, NY, 1953).
102. T. Matsuo, Preprints Atlantic Systems Conferences/Journal Chemical Society **20**, 895 (1979).
103. W. H. Stockmayer and M. Fixman, J. Polym. Sci. C 137 (1963).
104. J. W. Van Dyk, H. L. Frisch, and D. T. Wu, Ind. Eng. Chem. Prod. Res. Dev. **24**, 473 (1985).
105. J. E. Guillet, British Patent No. 1,331,429 (1973).
106. R. D. Newman and J. M. Prausnitz, J. Phys. Chem. **76**, 1492 (1972).
107. A. J. Manning and F. Rodriguez, J. Appl. Polym. Sci. **17**, 1651 (1973).
108. W. R. Song and D. W. Brownawell, Polym. Eng. Sci. **10**, 222 (1970).
109. B. A. Wolf, Macromol. Chem. **178**, 1869 (1977).
110. S. T. Bowden and W. J. Jones, Philos. Mag. **39**, 155 (1948).
111. C. W. Bunn, J. Polym. Sci. **16**, 323 (1955).
112. A. T. DiBenedetto, J. Polym. Sci. A **1**, 3459 (1963).
113. M. Dunkel, J. Phys. Chem. A **138**, 42 (1928).
114. R. A. Hayes, J. Appl. Polym. Sci. **5**, 318 (1961).
115. P. J. Hoftyzer and D. W. Van Krevelen, Paper No. III-15, presented at the International Symposium on Macromolecules of International Union of Pure and Applied Chemistry, Lyden, 1970.
116. K. L. Hoy, J. Paint Technol. **42**, 76 (1970).
117. A. E. Rheineck and K. F. Lin, J. Paint Technol. **40**, 611 (1968).
118. D. W. Van Krevelen, Fuel **44**, 229 (1965).
119. D. W. Van Krevelen and P. J. Hoftyzer, J. Appl. Polym. Sci. **11**, 2189 (1967).
120. A. H. Konstam and W. R. Fearheller, Jr., Am. Inst. Chem. Eng. J. **16**, 837 (1960).
121. D. W. Van Krevelen, *Properties of Polymers, Correlations with Chemical Structure 2nd ed.* (Elsevier Amsterdam, 1976).
122. R. L. Scott and M. Magat, J. Polym. Sci. **4**, 555 (1949).
123. P. J. Flory, J. Chem. Phys. **10**, 51 (1942).
124. P. J. Flory and J. Rehner, Jr., J. Chem. Phys. **11**, 512 (1943).
125. A. F. M. Barton, in *Polymer Cohesion Parameters and Polymer-Liquid Interaction Parameters, Polymer Yearbook 6*, edited by R. A. Pethrick, G. E. Zaikou, and T. Tsuruta, (Harwood Academic Publishers, New York, 1990), p. 94.
126. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 3rd ed. (Wiley, New York, 1989).
127. Allan F. M. Barton, *CRC Handbook of Solubility Parameters and Other Cohesion Parameters 2nd ed.* (CRC, Boca Raton, FL, 1991).
128. F. W. Billmeyer, Jr., *Textbook of Polymer Science*, 2nd ed. (Wiley-Interscience, New York, 1971).
129. A. G. Shvarts, Kolloid Z. **18**, 755 (1956).
130. A. V. Tobolsky, *Properties and Structure of Polymers* (Wiley, New York, 1960), pp. 64 and 66.
131. G. Gee, Trans. Inst. Rubber Ind. **18**, 266 (1943).
132. H. Mark and A. V. Tobolsky, *Physical Chemistry of High Polymers* (Interscience, New York, 1950), p. 263.
133. S. Arichi and S. Himuro, Polymer **30**, 686 (1989).
134. D. Mangaraj, S. Patra, and S. B. Rath, Makromol. Chem. **67**, 84 (1963).
135. D. Mangaraj, S. Patra, and S. Rashid, Makromol. Chem. **65**, 39 (1963).
136. J. E. G. Lipson and J. E. Guillet, J. Polym. Sci. Polym. Phys. Ed. **19**, 1199 (1981).
137. M. Lautout and M. Magat, Z. Phys. Chem. (Frankfurt) **16**, 292 (1958).
138. M. Roth, J. Appl. Polym. Sci. B Polym. Phys. **28**, 2715 (1990).
139. F. Vocks, J. Polym. Sci. A-2, 5319 (1964).
140. L. Mandelkern, private communication to H. Burrell, *Polymer Handbook*, 1st ed. (Interscience Publishers, New York, 1966).
141. M. M. Marugan, E. Perez, R. Benavente, A. Bello, and J. M. Perena, Europ. Polym. J. **28**, 1159 (1992).
142. D. Mangaraj, S. K. Bhatnagar, and S. B. Rath, Makromol. Chem. **67**, 75 (1963).
143. G. Gee, G. Allen, and G. Wilson, Polymer (London) **1**, 456 (1960).
144. K. K. Chee and S. C. Ng, J. Appl. Polym. Sci. **50**, 1115 (1993).
145. K. S. Siow, S. H. Goh, and K. S. Yap, Polym. Mater. Sci. Eng. **51**, 532 (1984).
146. R. S. Tillaev, M. Khasaukhanova, S. A. Tashmukhamedov, and Kh. U. Usmanov, J. Polym. Sci. C **39**, 107 (1972).
147. D. Mangaraj, S. Patra, P. C. Roy, and S. K. Bhatnagar, Makromol. Chem. **84**, 225 (1965).
148. B. C. Ho, W. K. Chin, and Y. D. Lee, J. Appl. Polym. Sci. **42**, 99 (1991).
149. A. Belfkira and J. P. Montheard, J. Appl. Polym. Sci. **51**, 1849 (1994).
150. S. M. Aharoni, J. Appl. Polym. Sci. **45**, 813 (1992).
151. T. Matsuuura, P. Blais, and S. Sourirajan, J. Appl. Polym. Sci. **20**, 1515 (1976).