18 The Future

Charles M. Hansen

ABSTRACT

Hansen solubility parameters (HSP) help to quantify the statements "like dissolves like" and "like seeks like." These parameters have found use in many fields of research and practice, primarily because their unique predictive capabilities are based on sound theoretical principles. HSP have extended the original Hildebrand single solubility parameter approach by quantitatively taking into account the molecular permanent dipole–permanent dipole and molecular hydrogen bonding (electron interchange) interactions. HSP and the Prigogine corresponding states theory of polymer solutions are mutually confirming with regard to treatment of specific interactions, as shown in Chapter 2. This is important, as it confirms that the HSP correlations must continue to include a constant not too different from the currently used "4" (or 0.25). This is necessary to differentiate between the atomic (δ_D) and the molecular (specific) interactions (δ_P and δ_H). Neglecting this differentiation will lead to misinterpretations. The geometric mean average for the interaction of unlike molecules is inherently used in the Hildebrand approach and in the HSP approach as well. This same mean must be used in the Prigogine corresponding states theory if agreement is to be found with the HSP correlations presented in this book. As the agreement is general, the conclusion must be that the geometric mean can be used to average not only dispersion interactions but also those attributable to permanent dipoles and to hydrogen bonding. These findings have been supported more recently by the statistical thermodynamics approach of Panayiotou and coworkers summarized in Chapter 3. This approach allows independent calculation of each of the three parameters.

Based on the large number of current uses of HSP, one can easily suppose that there are many more practical uses which remain to be discovered and developed. One need not necessarily extend its theoretical scope to accomplish this. The existing data can be used in a strictly empirical manner if so desired. However, a glimpse has been given of a very general energetic approach to systematically predict and control molecular interactions among many materials of widely different composition. The general predictions possible for these physical interactions have been demonstrated for both bulk phenomena (solubility, swelling, compatibility) and surface phenomena (adsorption, dewetting, spontaneous spreading). In the future, the theory should be explored and used with this general applicability in mind.

Problems and situations clearly needing further attention are discussed in the following.

INTRODUCTION

There are many matters related to HSP which still need clarification and expansion. Some limitations are clear, but others are not so clear. As this book is primarily directed toward the practitioner, the following discussions will start with more practical topics.

The first matter of concern is the availability of data. This handbook attempts to help improve this situation by publishing HSP for a larger number of liquids, about 1200, primarily in the Appendix, Table A.1. This handbook also contains new HSP correlations not present in the first edition. Many of these are given as examples in the text, and others are included in the Appendix, Table A.2. Other sources are discussed below.

The second matter of concern is how reliable the HSP data are and how accurately the correlations can predict the behavior of untested systems. Qualitative indications of this for the

data generated by the author are given in the relevant tables. In general correlation coefficients approach 1.0. This indicates perhaps only a few minor outliers in the correlations, as can be seen from those included in this handbook. There are very rarely major outliers, and these usually have another explanation for their behavior, such as very large molecular size, very small molecular size, reactions, or the like. The experience reported in Chapter 4, Table 4.4A, for the reliability of the "original Hansen" approach does not correspond to this experience. Normally there are perhaps 5 or 6 boundary solvents that are not predicted correctly out of about 100 test solvents in a correlation of experimental data. This was the case for the correlations presented in Table 5.1, rather than the ratio of 99 correct answers with 23 incorrect answers indicated in Table 4.4A. The reason for this discrepancy is not known, but if group contribution or other estimates are involved, especially for polymers, then the number of "errors" will increase.

A third point which is sometimes irritating is that the scope of the characterizations possible is limited to the cohesive energy spectrum of the test liquids. A situation is often met where only a few solvents having high solubility parameters dissolve a polymer which has still higher HSP. Similarly, only a few solvents may interact intimately with a surface which has very high HSP. These surfaces are clearly wet because of the lower surface tension of all of the liquids, but only a few with high HSP prolong suspension of finer particles, for example. The energy characteristics of such surfaces are apparently higher than those of any liquids which can be used to study them by these techniques. Very high cohesive energies lead to the formation of solids, so there are no pure liquids which can be used to test the very high energy materials. New thinking and new techniques are required to accurately characterize such high energy materials. A full understanding of the behavior of water, organometallic materials, and salt solutions might be helpful in these situations (see the following corresponding sections). The current practice is to extrapolate into the region of very high HSP using Chapter 1, Equation 1.9 which includes the constant "4." It is assumed that this constant is still valid, even for these very high energy characterizations. The given good solvents are often in the boundary region of the HSP spherical characterizations. The solubility of Dextran C (British Drug Houses)[1] is an example of this as shown in Table 18.1 and Table 18.2. See Chapter 5 and Chapter 7 for further discussion of this problem which is present for both polymers and particulate matter. In a sense, the problem is similar to measuring the surface tension of a surface which has such a high value that even water spontaneously spreads on it. One can only conclude that its surface tension is greater than that of water. In the present case, there is a model to extrapolate HSP to higher values than can be measured directly.

Another concern related to reliable HSP values is based on the fact that most chemicals in the intermediate molecular weight range, such as that characteristic of plasticizers, are soluble in almost all of the test liquids, except for, for example, glycerin, water, and hexane. It is impossible to establish the three HSP based on such data. One generally has to rely on group contribution methods or other calculations or comparisons, and there will be some uncertainty involved with this.

Once the necessary reliable HSP data are available, decisions and ideas are needed on how the data should be used. It is here that the existing theory and future extensions of it are most important. In many cases, engineering approximations leading to a systematic course of action have been possible using data which is currently available. One can often arrive at a prediction for expected behavior using the "like seeks like" principle, even though accurate numbers and an appropriate detailed theory may be lacking. It is hoped that this book will aid in the generation of still more HSP data having a uniformly high quality, such that the interactions among still more materials can be predicted. Logical applications for HSP will be found in self-assembling systems and in what is called nanotechnology, for example. One example is the self-stratifying paints discussed in Chapter 8. Another is the ultrastructure of cell walls in wood discussed in Chapter 15.

TABLE 18.1
Calculated Solubility Sphere for Dextran C Solubility

	The Solvents with Their Parameters					
Solvent	δ_D	δ_P	δ_H	SOLUB	RED	V
Acetone	15.5	10.4	7.0	0	1.454	74.0
Acetophenone	19.6	8.6	3.7	0	1.371	117.4
Aniline	19.4	5.1	10.2	0	1.241	91.5
Benzaldehyde	19.4	7.4	5.3	0	1.346	101.5
Benzene	18.4	0.0	2.0	0	1.776	89.4
1,3-Butanediol	16.6	10.0	21.5	0	1.054	89.9
1-Butanol	16.0	5.7	15.8	0	1.313	91.5
Butyl acetate	15.8	3.7	6.3	0	1.640	132.5
gamma-Butyrolactone	19.0	16.6	7.4	0	1.077	76.8
Carbon disulfide	20.5	0.0	0.6	0	1.756	60.0
Carbon tetrachloride	17.8	0.0	0.6	0	1.858	97.1
Chlorobenzene	19.0	4.3	2.0	0	1.601	102.1
Chloroform	17.8	3.1	5.7	0	1.556	80.7
m-Cresol	18.0	5.1	12.9	0	1.246	104.7
Cyclohexanol	17.4	4.1	13.5	0	1.312	106.0
Cyclohexanone	17.8	6.3	5.1	0	1.473	104.0
Diacetone alcohol	15.8	8.2	10.8	0	1.363	124.2
o-Dichlorobenzene	19.2	6.3	3.3	0	1.474	112.8
2,2-Dichlorodiethyl ether	18.8	9.0	5.7	0	1.313	117.2
Diethylene glycol	16.6	12.0	20.7	0	1.000	94.9
Diethyl ether	14.5	2.9	5.1	0	1.795	104.8
Dimethyl formamide	17.4	13.7	11.3	0	1.082	77.0
Dimethyl sulfoxide	18.4	16.4	10.2	1*	1.000	71.3
1,4-Dioxane	19.0	1.8	7.4	0	1.485	85.7
Dipropylene glycol	16.5	10.6	17.7	0	1.080	130.9
Ethanol	15.8	8.8	19.4	0	1.180	58.5
Ethanolamine	17.0	15.5	21.2	1	0.880	59.8
Ethyl acetate	15.8	5.3	7.2	0	1.559	98.5
Ethylene dichloride	19.0	7.4	4.1	0	1.416	79.4
Ethylene glycol	17.0	11.0	26.0	1*	1.003	55.8
Ethylene glycol monobutyl ether	16.0	5.1	12.3	0	1.406	131.6
Ethylene glycol monoethyl ether	16.2	9.2	14.3	0	1.211	97.8
Ethylene glycol monomethyl ether	16.2	9.2	16.4	0	1.170	79.1
Formamide	17.2	26.2	19.0	1	0.915	39.8
Glycerol	17.4	12.1	29.3	1	0.991	73.3
Hexane	14.9	0.0	0.0	0	2.037	131.6
Isophorone	16.6	8.2	7.4	0	1.410	150.5
Methanol	15.1	12.3	22.3	0	1.144	40.7
Methylene dichloride	18.2	6.3	6.1	0	1.411	63.9
Methyl isobutyl carbinol	15.4	3.3	12.3	0	1.517	127.2
Methyl isobutyl ketone	15.3	6.1	4.1	0	1.679	125.8
Nitrobenzene	20.0	8.6	4.1	0	1.336	102.7
Nitromethane	15.8	18.8	5.1	0	1.399	54.3
2-Nitropropane	16.2	12.1	4.1	0	1.479	86.9
Propylene carbonate	20.0	18.0	4.1	0	1.172	85.0
Propylene glycol	16.8	9.4	23.3	0	1.053	73.6

TABLE 18.1 (CONTINUED)
Calculated Solubility Sphere for Dextran C Solubility

Solvent	δ_D	δ_P	δ_H	SOLUB	RED	V
Tetrahydrofuran	16.8	5.7	8.0	0	1.450	81.7
Tetrahydronaphthalene	19.6	2.0	2.9	0	1.618	136.0
Toluene	18.0	1.4	2.0	0	1.744	106.8
Trichloroethylene	18.0	3.1	5.3	0	1.560	90.2

Note: δ_D = 24.3 δ_P = 19.9 δ_H = 22.5 Ro = 17.4 FIT = 0.999 NO = 50.

HANSEN SOLUBILITY PARAMETER DATA AND DATA QUALITY

The author and others including most solvent suppliers and some paint companies (at least) have databases including HSP data for solvents and HSP correlations for polymer solubility etc. Tables of HSP data for many materials are also included in standard reference works.[2–5] There is still a tendency to regard the contents of such databases as proprietary information for the benefit of the owner and/or his/her customers. Exxon, for example, has indicated a computer program based on HSP where data for over 500 solvents and plasticizers, 450 resins, and 500 pesticides are included.[6,7] The use of these parameters is becoming so commonplace that, in many studies, the δ_D, δ_P, and δ_H parameters often appear without any specific reference to where they came from or what they actually represent.

The solvent listing in the Appendix, Table A.1 includes the previously published set of some 240 solvents which have appeared earlier in several sources.[2,4,5,8,9] Some of the values have been revised over the years. The materials given in dark type have had some degree of experimental verification. All the others are based on calculations only. The methods described in Chapter 1 were used, although in many cases data was lacking to such an extent that group contributions were used. In some cases data for whole, smaller molecules whose HSP are known can be used to derive group contributions for estimating the HSP of larger molecules wherein they appear as a part. There are many additions to the original set of data. The calculated values have been checked against performance data reported in the literature where this has been possible. An example is the solubility data reported for poly(vinylidene chloride) (PVDC).[10] Appendix, Table A.1 also includes HSP for a number of low molecular weight solids. Low molecular weight solids with relatively low melting points have been treated as if they were liquids for extrapolation of latent heats to 25°C. This seems to be satisfactory, and it is consistent with the treatment of high boiling liquids. See Chapter 1 for details of the calculations. The first edition of this handbook contained over 800 HSP values for chemicals. This has been expanded to about 1200 values in the second edition.

HSP correlations in addition to those given in connection with examples in the text are included in Appendix, Table A.2. Only data judged (reasonably) reliable are reported. There are limitations on the accuracy of the HSP data derived from Burrell's solvent range studies reported in standard reference works,[2,11,12] but many correlations based on these data are included for reference anyway. The solvent range chosen for the studies does not completely fill out the possibilities selection of different liquids would have allowed. The problem of estimating a sphere based on limited data which do not experimentally define the whole sphere becomes more acute. This problem is greatest for polymers with high HSP, as not only is there a lack of possible data, but much of the volume of the HSP sphere is located where there are no liquids. The cohesion energies are so high that no liquids are possible and only solids are present. An example of a good HSP correlation from the solvent range studies is that of polyethylene sulfide. This polymer has relatively low HSP, and the solvents in the test series provide nonsolvents at higher HSP than those of the polymer to locate the boundaries with sufficient accuracy. This is shown in Tables 18.3 and 18.4. A comparison of

TABLE 18.2
Calculated Solubility Sphere for Dextran C Solubility

			The Solvents with Their Parameters			
Solvent	δ_D	δ_P	δ_H	SOLUB	RED	V
Succinic anhydride	18.6	19.2	16.6		0.739	66.8
Triethanolamine	17.3	22.4	23.3		0.819	133.2
Dimethyl sulfone	19.0	19.4	12.3		0.846	75.0
Ethylene cyanohydrin	17.2	18.8	17.6		0.866	68.3
2-Pyrolidone	19.4	17.4	11.3		0.867	76.4
Ethanolamine	17.0	15.5	21.2	1	0.880	59.8
Formamide	17.2	26.2	19.0	1	0.915	39.8
Diethanolamine	17.2	10.8	21.2		0.972	95.9
1,3-Butanediol	18.0	8.4	21.0		0.984	87.5
Glycerol	17.4	12.1	29.3	1	0.991	73.3
Dimethyl sulfoxide	18.4	16.4	10.2	1	1.000	71.3
Diethylene glycol	16.6	12.0	20.7	0	1.000	94.9
Ethylene glycol	17.0	11.0	26.0	1*	1.003	55.8
Propylene glycol	16.8	9.4	23.3	0	1.053	73.6
1,3-Butanediol	16.6	10.0	21.5	0	1.054	89.9
Diethylenetriamine	16.7	13.3	14.3		1.063	108.0
Triethyleneglycol	16.0	12.5	18.6		1.068	114.0
gamma-Butyrolactone	19.0	16.6	7.4	0	1.077	76.8
Dipropylene glycol	16.5	10.6	17.7	0	1.080	130.9
Dimethyl formamide	17.4	13.7	11.3	0	1.082	77.0
Allyl alcohol	16.2	10.8	16.8		1.117	68.4
o-Methoxyphenol	18.0	8.2	13.3		1.121	109.5
Hexamethylphosphoramide	18.5	8.6	11.3		1.132	175.7
Ethylenediamine	16.6	8.8	17.0		1.136	67.3
Methanol	15.1	12.3	22.3	0	1.144	40.7
Furfuryl alcohol	17.4	7.6	15.1		1.144	86.5
Trimethylphosphate	16.7	15.9	10.2		1.147	115.8
Benzyl alcohol	18.4	6.3	13.7		1.152	103.6
Ethylene carbonate	19.4	21.7	5.1		1.152	66.0
Phenol	18.0	5.9	14.9		1.167	87.5
Ethylene glycol monomethyl ether	16.2	9.2	16.4	0	1.170	79.1
Propylene carbonate	20.0	18.0	4.1	0	1.172	85.0
Ethanol	15.8	8.8	19.4	0	1.180	58.5
1,1,2,2-Tetrabromoethane	22.6	5.1	8.2		1.199	116.8
Ethylene glycol monoethyl ether	16.2	9.2	14.3	0	1.211	97.8
N,N-Dimethyl acetamide	16.8	11.5	10.2		1.215	92.5
3-Chloro-1-propanol	17.5	5.7	14.7		1.216	84.2
Hexylene glycol	15.7	8.4	17.8		1.219	123.0
Methyl-2-pyrrolidone	18.0	12.3	7.2		1.220	96.5
Furfural	18.6	14.9	5.1		1.230	83.2
Aniline	19.4	5.1	10.2	0	1.241	91.5
m-Cresol	18.0	5.1	12.9	0	1.246	104.7
1-Propanol	16.0	6.8	17.4		1.250	75.2
Benzoic acid	18.2	6.9	9.8		1.258	100.0
Triethylphosphate	16.7	11.4	9.2		1.259	171.0
Quinoline	19.4	7.0	7.6		1.265	118.0
Diethylene glycol monoethyl ether	16.1	9.2	12.2		1.272	130.9
Acetic anhydride	16.0	11.7	10.2		1.277	94.5

TABLE 18.2 (CONTINUED)
Calculated Solubility Sphere for Dextran C Solubility

Solvent	δ_D	δ_P	δ_H	SOLUB	RED	V
Tricresyl phosphate	19.0	12.3	4.5		1.277	316.0
Formic acid	14.3	11.9	16.6		1.284	37.8
Tetramethylurea	16.7	8.2	11.0		1.285	120.4

Note: δ_D = 24.3 δ_P = 19.9 δ_H = 22.5 Ro = 17.4 FIT = 0.999 NO = 50.

the solvents included in Table 18.3 with those in Table 18.1 shows which ones are lacking in the high HSP range. An example of a poor correlation using solvent range data is that of the solubility of polyvinyl alcohol. Only two of the solvents, ethanol and 2-propanol, dissolve it. This leads to a correlation with the following data: $\delta_D;\delta_P;\delta_H;$Ro equal to 17.0;9.0;18.0;4.0 in MPa$^{1/2}$ with a perfect fit for two good solvents out of 56 in the set of data. The use of these data is not recommended. Ro is clearly too small by comparison with Ro found in HSP correlations for solubility for other water-soluble polymers.

One of the problems with some of the reported correlations in the Appendix, Table A.2 is that the data on which they are based were not generated for this purpose. There are shortcomings in terms of lack of full coverage of the HSP space as well as in the total number of liquids for which there are data. Note that a standard set of test solvents such as that used in Table 18.1 takes full coverage into account. However, some of these liquids must be handled with care for reasons of toxicity. Data for chemical resistance, permeation, and other phenomena related to solubility which can be correlated with HSP are practically never accumulated with an HSP correlation in mind. This does not prevent use of such data as demonstrated elsewhere in this book, but it does place some limitations on the reliability of the predictions obtainable from the correlations. A qualitative indication of the reliability of the correlations is given for this reason.

Reliable HSP data for many polymers of practical importance are not available at this time. It would seem advisable for raw material suppliers to determine the HSP for their relevant products in a reliable manner and to publish these data on their product data sheets or elsewhere. Including them in a possible future edition of this book may also be a possibility.

For the sake of completeness, a couple of warnings are appropriate before proceeding to the next section. As noted in Chapter 1, the three partial solubility parameters tabulated by Hoy[13,14] are not compatible with those of the author. As discussed in the next section, the group contribution procedure presented by van Krevelen and Hoftyzer[15] does not give satisfactory agreement with the procedures given in Chapter 1. Finally, water (or its mixtures) should not be included currently in any HSP correlations without a very careful analysis of the results. The small molecular volume, exceptionally high δ_H parameter, and tendency to self-associate depending on the local environment all lead to the likely result that water will be an outlier for the correlation. This results in HSP values which are less reliable, and have lower predictive ability than had water been neglected. Mixtures of organic solvents with water are still more problematic when used as test liquids (see Figure 18.1 and the following discussion). A goal of future work should be to be able to account for the behavior of water in a reliable manner, such that it can be included in studies leading to HSP correlations. The HSP values for water found from the correlation for total water solubility reported in Chapter 1 (Table 1.3) appear promising for some applications where the HSP values for water as a single molecule are clearly not applicable.

TABLE 18.3
Calculated Solubility Sphere for Polyethylenesulfide

Solvent	δ_D	δ_P	δ_H	SOLUB	RED	V
Acetic acid	14.5	8.0	13.5	0	3.352	57.1
Acetone	15.5	10.4	7.0	0	2.285	74.0
Acetonitrile	15.3	18.0	6.1	0	3.793	52.6
Aniline	19.4	5.1	10.2	0	2.125	91.5
Benzene	18.4	0.0	2.0	1	0.973	89.4
1-Butanol	16.0	5.7	15.8	0	3.462	91.5
sec-Butyl acetate	15.0	3.7	7.6	0	1.898	133.6
Butyraldehyde	14.7	5.3	7.0	0	1.947	88.5
Carbon tetrachloride	17.8	0.0	0.6	0	1.006	97.1
Chlorobenzene	19.0	4.3	2.0	1	0.600	102.1
p-Chlorotoluene	19.1	6.2	2.6	0*	0.869	118.3
m-Cresol	18.0	5.1	12.9	0	2.631	104.7
Cyclohexane	16.8	0.0	0.2	0	1.155	108.7
Cyclopentanone	17.9	11.9	5.2	0	2.107	89.1
1,2-Dichloro ethylene (cis)	17.0	8.0	3.2	1*	1.123	75.5
o-Dichlorobenzene	19.2	6.3	3.3	1	0.954	112.8
2,2-Dichlorodiethyl ether	18.8	9.0	5.7	0	1.605	117.2
Dichlorodifluoromethane (Freon 12)	12.3	2.0	0.0	0	2.771	92.3
Dichloromonofluoromethane	15.8	3.1	5.7	0	1.308	75.4
Diethyl amine	14.9	2.3	6.1	0	1.744	103.2
Diethyl ether	14.5	2.9	5.1	0	1.772	104.8
Diethylene glycol	16.6	12.0	20.7	0	4.970	94.9
Di-isobutyl ketone	16.0	3.7	4.1	0*	0.993	177.1
N,N-Dimethyl acetamide	16.8	11.5	10.2	0	2.752	92.5
Dimethyl formamide	17.4	13.7	11.3	0	3.286	77.0
1,4-Dioxane	19.0	1.8	7.4	0	1.480	85.7
Ethanol	15.8	8.8	19.4	0	4.476	58.5
Ethyl acetate	15.8	5.3	7.2	0	1.604	98.5
2-Ethyl hexanol	15.9	3.3	11.8	0	2.521	156.6
Ethylene carbonate	19.4	21.7	5.1	0	4.491	66.0
Ethylene glycol	17.0	11.0	26.0	0	6.077	55.8
Ethylene glycol monobutyl ether	16.0	5.1	12.3	0	2.634	131.6
Ethylene glycol monoethyl ether	16.2	9.2	14.3	0	3.325	97.8
Furfural	18.6	14.9	5.1	0	2.825	83.2
Furfuryl alcohol	17.4	7.6	15.1	0	3.286	86.5
Glycerol	17.4	12.1	29.3	0	6.916	73.3
Isoamyl acetate	15.3	3.1	7.0	0	1.699	148.8
Isoamyl alcohol	15.8	5.2	13.3	0	2.898	109.4
Isopropyl acetate	14.9	4.5	8.2	0	2.043	117.1
Methanol	15.1	12.3	22.3	0	5.483	40.7
Methyl acetate	15.5	7.2	7.6	0	1.919	79.7
Methyl ethyl ketone	16.0	9.0	5.1	0	1.697	90.1
Methyl n-amyl ketone	16.2	5.7	4.1	0	1.019	139.8
Nitroethane	16.0	15.5	4.5	0	3.038	71.5
Nitromethane	15.8	18.8	5.1	0	3.852	54.3
Octane	15.5	0.0	0.0	0	1.551	163.5

TABLE 18.3 (CONTINUED)
Calculated Solubility Sphere for Polyethylenesulfide

Solvent	δ_D	δ_P	δ_H	SOLUB	RED	V
1-Octanol	17.0	3.3	11.9	0	2.401	157.7
Pentane	14.5	0.0	0.0	0	1.933	116.2
1-Pentanol	15.9	4.5	13.9	0	3.005	108.6
2-Propanol	15.8	6.1	16.4	0	3.642	76.8
Propionitrile	15.3	14.3	5.5	0	2.948	70.9
Propylene carbonate	20.0	18.0	4.1	0	3.655	85.0
Styrene	18.6	1.0	4.1	1	0.913	115.6
t-Butyl alcohol	15.2	5.1	14.7	0	3.317	95.8
Tetrahydronaphthalene	19.6	2.0	2.9	1	0.996	136.0
Xylene	17.6	1.0	3.1	1	0.724	123.3

Note: δ_D = 17.8; δ_P = 3.8; δ_H = 2.2; Ro = 4.1; FIT = 0.981; NO = 56.

GROUP CONTRIBUTION METHODS

Suggested calculation procedures to arrive at the HSP for solvents are given in Chapter 1. The group contribution methods need expansion with new groups. New group contributions should be checked for reliability of the predictions in some way, which is not always possible within the timeframe of most projects. The group contribution values consistently used by the author are reported in Chapter 1. Values added over the years are appended to the original table which was attributable to Beerbower.[4,17,18] Barton has also collected many tables of group contributions for various purposes.[2] As stated previously, the group contributions tabulated by van Kevelen[15] have not been found reliable. The δ_D parameter, in particular, is not predicted well. The author chose not to use these at an early date, although many other authors have chosen to do so. The use of various predictive methods which arrive at different results has always been a problem. Koenhen and Smolders[19] evaluated various equations for predicting HSP.

Methods for reliable a priori calculation of the HSP for polymers are not available. This is a serious shortcoming. The author has tried several times to calculate the HSP for individual polymers using the same group contributions suggested for the liquids, and almost every time has ultimately resorted to experiment. Calculation of the radius of interaction is a particular problem in this respect. This is definitely an area requiring attention. Chapter 2 discusses some of the factors which must be taken into account when calculating the radius of interaction. If one consistently uses the same method of estimating HSP, it can be assumed that some of the inherent errors will not affect relative evaluations. Utracki and coworkers[20] estimated HSP for a number of polymers assuming their δ_D parameters were not different and group contributions for the δ_P and δ_H parameters. This is discussed in Chapter 5.

POLYMERS AS POINTS — SOLVENTS AS SPHERES

One way to possibly improve predicting the behavior of polymers is to consider them as points (or more accurately, spheres, with very small radii of interaction that depend on molecular weight) rather than as spheres with large radii, as is presently done. A given solvent is assigned a rather large radius of interaction. This radius is larger for smaller molar volume in this inverted approach. This idea was presented many years ago,[8,21] but it has never been fully explored. The first indications were that there seemed to be no real benefit in terms of improved reliability of predictions for polymer solubility in organic solvents, which was of primary interest, so there was no need to start

TABLE 18.4
Calculated Solubility Sphere for Polyethylenesulfide

Solvent	δ_D	δ_P	δ_H	SOLUB	RED	V
Chlorobenzene	19.0	4.3	2.0	1	0.600	102.1
Xylene	17.6	1.0	3.1	1	0.724	123.3
p-Chlorotoluene	19.1	6.2	2.6	0*	0.869	118.3
Styrene	18.6	1.0	4.1	1	0.913	115.6
o-Dichlorobenzene	19.2	6.3	3.3	1	0.954	112.8
Benzene	18.4	0.0	2.0	1	0.973	89.4
Di-isobutyl ketone	16.0	3.7	4.1	0*	0.993	177.1
Tetrahydronaphthalene	19.6	2.0	2.9	1	0.996	136.0
Carbon tetrachloride	17.8	0.0	0.6	0	1.006	97.1
Methyl n-amyl ketone	16.2	5.7	4.1	0	1.019	139.8
1,2-Dichloro ethylene (cis)	17.0	8.0	3.2	1*	1.123	75.5
Cyclohexane	16.8	0.0	0.2	0	1.155	108.7
Dichloromonofluoromethane	15.8	3.1	5.7	0	1.308	75.4
1,4-Dioxane	19.0	1.8	7.4	0	1.480	85.7
Octane	15.5	0.0	0.0	0	1.551	163.5
Ethyl acetate	15.8	5.3	7.2	0	1.604	98.5
2,2-Dichlorodiethyl ether	18.8	9.0	5.7	0	1.605	117.2
Methyl ethyl ketone	16.0	9.0	5.1	0	1.697	90.1
Isoamyl acetate	15.3	3.1	7.0	0	1.699	148.8
Diethyl amine	14.9	2.3	6.1	0	1.744	103.2
Diethyl ether	14.5	2.9	5.1	0	1.772	104.8
sec-Butyl acetate	15.0	3.7	7.6	0	1.898	133.6
Methyl acetate	15.5	7.2	7.6	0	1.919	79.7
Pentane	14.5	0.0	0.0	0	1.933	116.2
Butyraldehyde	14.7	5.3	7.0	0	1.947	88.5
Isopropyl acetate	14.9	4.5	8.2	0	2.043	117.1
Cyclopentanone	17.9	11.9	5.2	0	2.107	89.1
Aniline	19.4	5.1	10.2	0	2.125	91.5
Acetone	15.5	10.4	7.0	0	2.285	74.0
1-Octanol	17.0	3.3	11.9	0	2.401	157.7
2-Ethyl hexanol	15.9	3.3	11.8	0	2.521	156.6
m-Cresol	18.0	5.1	12.9	0	2.631	104.7
Ethylene glycol monobutyl ether	16.0	5.1	12.3	0	2.634	131.6
N,N-Dimethyl acetamide	16.8	11.5	10.2	0	2.752	92.5
Dichlorodifluoromethane (Freon 12)	12.3	2.0	0.0	0	2.771	92.3
Furfural	18.6	14.9	5.1	0	2.825	83.2
Isoamyl alcohol	15.8	5.2	13.3	0	2.898	109.4
Propionitrile	15.3	14.3	5.5	0	2.948	70.9
1-Pentanol	15.9	4.5	13.9	0	3.005	108.6
Nitroethane	16.0	15.5	4.5	0	3.038	71.5
Dimethyl formamide	17.4	13.7	11.3	0	3.286	77.0
Furfuryl alcohol	17.4	7.6	15.1	0	3.286	86.5
t-Butyl alcohol	15.2	5.1	14.7	0	3.317	95.8
Ethylene glycol monoethyl ether	16.2	9.2	14.3	0	3.325	97.8
Acetic acid	14.5	8.0	13.5	0	3.352	57.1
1-Butanol	16.0	5.7	15.8	0	3.462	91.5
2-Propanol	15.8	6.1	16.4	0	3.642	76.8
Propylene carbonate	20.0	18.0	4.1	0	3.655	85.0

TABLE 18.4 (CONTINUED)
Calculated Solubility Sphere for Polyethylenesulfide

Solvent	δ_D	δ_P	δ_H	SOLUB	RED	V
Acetonitrile	15.3	18.0	6.1	0	3.793	52.6
Nitromethane	15.8	18.8	5.1	0	3.852	54.3
Ethanol	15.8	8.8	19.4	0	4.476	58.5
Ethylene carbonate	19.4	21.7	5.1	0	4.491	66.0
Diethylene glycol	16.6	12.0	20.7	0	4.970	94.9
Methanol	15.1	12.3	22.3	0	5.483	40.7
Ethylene glycol	17.0	11.0	26.0	0	6.077	55.8
Glycerol	17.4	12.1	29.3	0	6.916	73.3

Note: $\delta_D = 17.8$; $\delta_P = 3.8$; $\delta_H = 2.2$; Ro = 4.1; FIT = 0.981; NO = 56.

all over again with this inverted system. On the other hand, there may be advantages in terms of more reliable prediction of polymer–polymer miscibility, for example. This was not explored. The requirement of polymer miscibility will be that the respective points (very small spheres) for the polymers must be very close to each other; comparing distances between small spheres is relatively easy. This type of comparison is sometimes difficult to make in the present approach where the degree of overlapping of rather large spheres is used to estimate polymer–polymer miscibility. No fixed rules of thumb have been established to estimate how much overlap is required for miscibility. However, guidelines for improving polymer–polymer miscibility are easily found in the present approach. These include selection of an improved solvent, reduction of polymer molecular weight, and modification of a polymer's HSP in a desired direction based on the HSP group contributions of its repeating unit or comonomers, for example.

Traditionally, solvents are considered as points. This is practical and almost necessary from an experimental point of view as most solvents are so miscible as to not allow any experimental characterization in terms of a solubility sphere. An exception to this is the data for water reported in Table 1.3. The HSP reported here are the center points of HSP spheres where the good solvents are either those that are completely miscible or those that are miscible to only 1% or more.

CHARACTERIZING SURFACES

The characterization of surfaces with HSP, or perhaps more correctly cohesion parameters (having exactly the same numerical values), is still in its infancy. This possibility was demonstrated many years ago, however.[22] As shown in Chapters 6 and 7, this type of approach can lead to a new understanding of surface phenomena, which in turn allows systematic study and design of surfaces for desired behavior.

Data on surface characterizations, in addition to that in Chapter 6 and Chapter 7, are not provided here. This is primarily because such data are lacking but also because surface cohesion parameters may not be reflected by nominal bulk composition. The same basic pigment or filler, for example, can have widely different surface cohesion parameters, depending on how it has been surface treated. Neither has the effect of adsorbed water been clarified. Likewise, a surface characteristic for a polyvinyl chloride or a polyethylene cannot be expected to be valid for all polymers normally said to be of these compositions. There may also be additives which have different compositions and which may have migrated to the surfaces.

It appears that the relative simplicity of the surface characterizations discussed in this book would lead to their wider use. One current problem is that blindly entering wetting or spontaneous spreading data into the usual computer routine for finding the HSP values often leads to negative
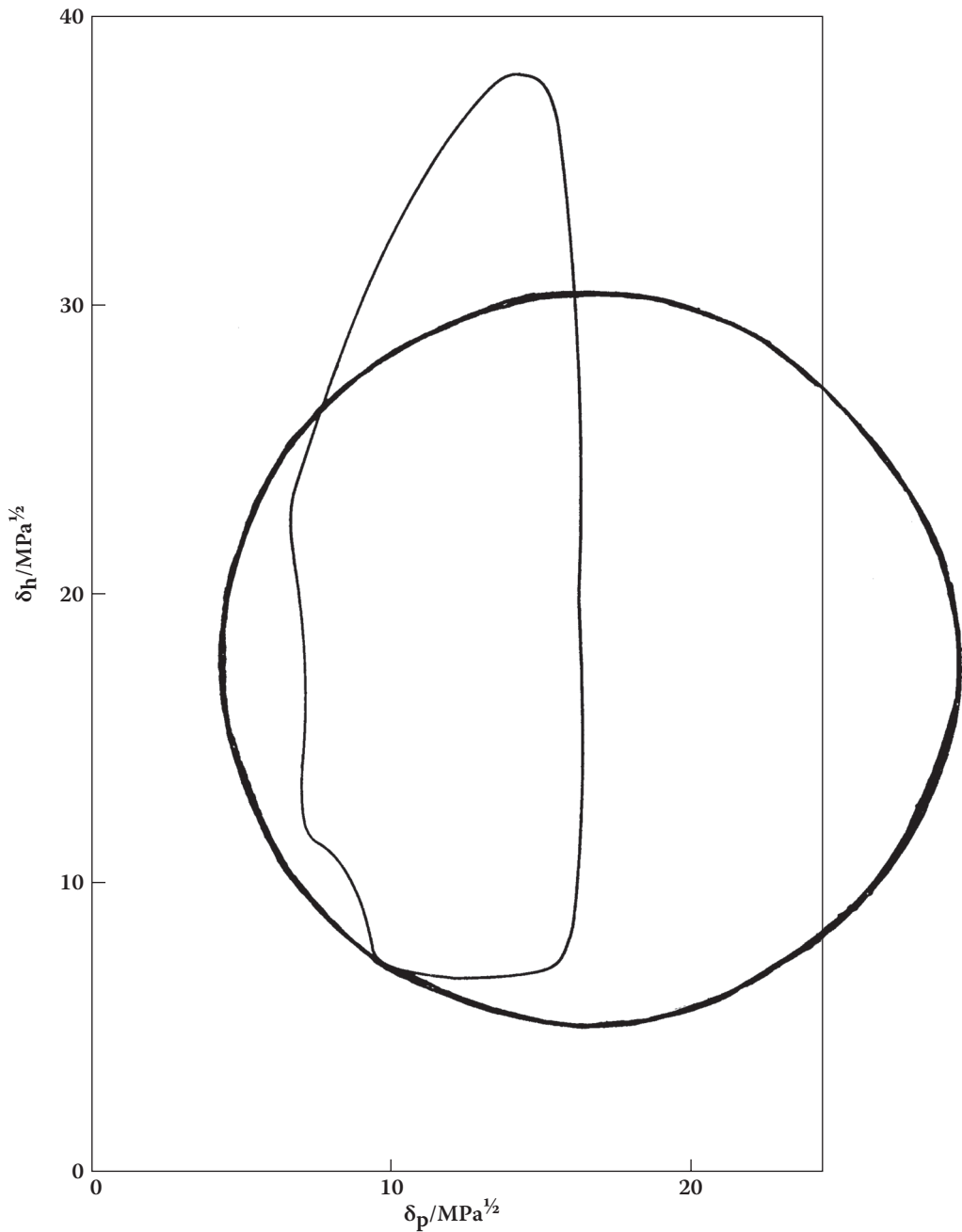
FIGURE 18.1 HSP plot of characterization of Rhodamin FB (C.I. Basic Violet 10) showing potential problems with incorporation of water mixtures as test solvents (see text for discussion). (From Riedel, G., *Farbe und Lack*, 82(4), 281–287, 1976. With permission.)

numbers for one or more of them. This was discussed in Chapter 6. Currently, the best approach is to compare plots or even to just compare tabulated data for the test solvents to determine where two surfaces differ in affinities. Guides for action can also be found by simple comparison of the HSP of those solvents which show a difference in behavior. A more systematic approach for the use of cohesion parameters to describe surface phenomena would be desirable.

MATERIALS AND PROCESSES SUGGESTED FOR FURTHER ATTENTION

Examples of the use of HSP for many types of materials and phenomena have been presented in earlier chapters. Some special types of materials are singled out here as worthy of still more attention in the near future. These include surface active agents, water, gases, organic and inorganic salts, organometallic materials, and aromatic (fragrances) materials. The uptake of potentially dangerous chemicals in recyclable packaging also needs attention. An additional area of interest may be found in that many commonly used reaction solvents have similar HSP. These include dimethyl sulfoxide, dimethyl formamide, dimethyl acetamide, and sulfolane, for example. It seems unlikely that this is a coincidence. It could be that the solubility of an activated species having high polarity (δ_P) and moderate hydrogen bonding (δ_H) is determining the reaction rate(s). Still another area of major interest is the systematic formulation of filled systems using HSP. This is also still in its infancy. Pigments and fillers need to be characterized. Several of these applications are discussed in more detail below. Surface active materials have remained essentially untouched in terms of HSP, although Beerbower started on this many years ago.[8,17,23]

SURFACE ACTIVE AGENTS

Surface active agents have not been systematically characterized by HSP yet, although Beerbower has developed some aspects of a theory for given situations.[8,17,23] The statement "like seeks like" indicates that surface active agents should be extensively treated in terms of HSP. Each end of such molecules will require its own set of HSP, as demonstrated by the example of lithium stearate, discussed later in the Organometallic Compounds section (Figure 18.3).

An example to help illustrate the type of prediction possible is to try to answer the question of where the hydrophobic end of a given surfactant will tend to preferentially reside. An aliphatic end group would have lower affinity for polystyrene, for example, than an aromatic one. Octane will not dissolve polystyrene, whereas toluene will. This is reflected by their cohesion energy parameters. This same reasoning applies to other polymers. A surfactant with a fluorinated end will not dissolve in many polymers where a hydrocarbon end will. The cohesion energy parameters characteristic of fluorocarbons are too low. Although these examples are obvious to those skilled in the science of surfaces, they point to the possibility of quantifying affinities of surface active materials in terms of the cohesion energy parameters of their respective end groups. Those familiar with cohesion energy parameters can already discern differences that may improve the chances of success. The data in Chapter 11 confirm that differences in HSP are critical if soils are to be removed effectively. HSP for surfactants can be assigned by experiment or by the methods described in the next paragraph.

Each surfactant must be assigned three sets of HSP. The first is for the hydrophobic end, the second is for the hydrophilic end, and the third is for the molecule as a whole. Figure 18.3 confirms the need for the first two characterizations, and the third one is required for predictions when the whole molecule is soluble in the system. Even in a completely dissolved condition, one anticipates some degree of orientation of the ends of the surfactant molecule toward regions of similar HSP. The HSP for the hydrophobic end can be estimated by the methods discussed in Chapter 1, with group contributions, or by simple comparison with similar (usually) hydrocarbon molecules of the same size. Barton has collected group contributions that can also be used in connection with the

different ends of surface active agents.[2]   The HSP of the hydrophilic end can be estimated by comparison with existing HSP of, for example, sucrose or other water soluble entity, organic salts (see below), inorganic salts (see below), polyethylene oxide or polyethylene glycol, or whatever resembles this end best. Experiments are preferred, of course, and the estimation for given inorganic salts is still uncertain. When a surfactant denatures a protein, there will be some similarity between the HSP of the protein or urea, if this also denatures the protein (see Chapter 15), and the HSP of the hydrophilic end of the surfactant. If enough data of this kind can be generated, the HSP of the surfactant can be experimentally confirmed. The estimation for the molecule as a whole involves combining the two sets of HSP for the ends. It is thought that this is best done by averaging using estimated molecular volumes for the respective ends relative to the molecular volume of the whole molecule.

In closing this section, it can also be repeated that thermodynamic surface and interfacial phenomena correlate with HSP. This has been amply shown in Chapter 6 and Chapter 7. The kinetics of the situation may also be important. Chapter 16 discusses adsorption and absorption in polymer surfaces where there is a surface resistance. There will also be some form of interfacial or boundary layer resistance influencing the adsorption and absorption of surfactants into soils, for example. If the HSP do not match sufficiently well, adsorption and absorption will presumably not occur as readily as when the HSP do match to within some required limit for the desired effect, as shown in Chapter 11. The size and shape of the adsorbing/absorbing entity is also presumed to be important from a kinetic point of view, as demonstrated by the examples in Chapter 16.

SURFACE MOBILITY (SELF-ASSEMBLY)

The rule of thumb that "like seeks like" can be very useful in understanding the structure of complicated systems. That this type of consideration can lead to useful results can be seen in the way that the behavior of wood polymers and the ultrastructure of cell walls in wood was treated in Chapter 13 and in much more detail by Hansen and Björkman.[24] Hemicelluloses appear to function much like surfactants with the backbone and those side chains containing hydroxyl groups favoring placement toward cellulose (or their own kind). Hemicellulose side chains containing acetyl, acid, or ether groups are expected to favor orientation toward lignin regions. In this example, it is interfacial mobility that is in focus, and it can be expected that the orientations may be changed with the transport or presence of other materials such as water through a given local environment. These predictions and inferences appear to agree with what is expected or has been established by independent measurement, but it is too early to say that confirmation has been obtained independently. The treatment of different segments of block copolymers as separate entities is a related endeavor where more quantitative predictions of compatibility should be possible. It is known that additions of a block of polymer C to both polymer A and polymer B improves their chances of compatibility (at some molecular level). The association of blocks of polymers is also the basis for the thermoplastic elastomers (TPE). These are made with a wide variety of different immiscible (hard and soft) blocks where the phase separation is critical to performance. Typical examples include the styrene/butadiene/styrene block copolymer (SBS), the polyether/polyamide block copolymer (PEBA), and polyurethanes combined with polyethers or polyesters (TPU). Some types are also vulcanized to improve properties.

The rotation of some hydrophobic materials to become more hydrophilic when in contact with water is still another example of like seeking like. Peat moss is an example. A drop of water initially pearls on the surface but shortly thereafter disappears into the interior in a spontaneous manner. The peat moss has become hydrophilic (but returns to the hydrophobic state on drying again). This phenomena was actually employed to develop an electrodeposition coating for an evaporator where film-wetting by water was required for good evaporation efficiency.[25] After several hours of exposure of a fresh coating to water, the static contact angles with water disappeared and a coherent water film was obtained.

Many surface phenomena can be understood from the preferences of given segments or materials to seek out regions of similar HSP. Some inferences may be possible from the studies performed on compatible (or nearly compatible) polymers. The HSP data leading to formulation of self-stratifying coatings also provides useful information[26] (see also Chapter 6). Systematic studies of these effects are badly needed. One such study[27] confirmed that the rotation ability (mobility) of aging polymer surfaces could be followed by measuring the (static) receding contact angle of water. Aging can be expected to lead to increased oxygenation and perhaps also to a decrease in average molecular weight. These effects both contribute to the tendency/ability for oxygenated species attached to an otherwise more hydrophobic polymer to rotate into an applied water droplet. When the (static) receding contact angle for water was measured, it fell with exposure time/aging at shorter times, whereas the (static) advancing contact remained constant. At longer exposure times, when the surface was oxygenated to a greater extent, the advancing contact angle also started to fall.

Surface mobility also has an important role in biological processes, as described in Chapter 15. The orientation of molecules to allow given segments to locate in regions of similar HSP is presumed to be a general phenomenon. Hydrophilic bonding (usually referred to in the present context as intermolecular hydrogen bonding) is responsible for the configurations of proteins in water. The proteins that can be dissolved in mixtures of water and urea or given salts, for example, are no longer "hydrogen bonded" in the conventional usage of the term, as they are now truly dissolved by an effectively good solvent that can also dissolve these segments/bonding sites. The usual solvent, water, does not have the correct set of HSP to truly dissolve these segments of the protein molecules. The urea additions correct for this deficiency, and the protein is said to be denatured in the process. The concept of hydrophilic (hyperphilic?) bonding, which is the opposite of hydrophobic bonding, is discussed in more detail with examples in Chapter 15. These phenomena also point to the use of urea or urea groups to improve biocompatibility.

Many of the concepts discussed here are directly applicable for self-assembling systems and to procedures and products within the concepts of nanotechnology.

WATER

The current treatment of the HSP for water discussed in Chapter 1 and Chapter 15 needs confirmation and/or modification. As noted earlier on several occasions, water is very special because of its low molecular volume, its very high δ_H parameter for a liquid, and its tendency to self-associate or to associate with other materials forming special structures. The HSP correlations for the solubility of solvents in water presented in Chapter 1, Table 1.3 have not been tested extensively as yet, but do seem promising. They are clearly useful to make predictions for the solubility of untested solvents in water, but whether or not these HSP data for water can be used in a larger context remains to be determined. General behavior can be predicted, but can specific behavior be predicted? More research is needed in this area, but, in the meantime, water can be considered as having (at least) duality. Sometimes it acts like a single molecule, and sometimes it acts as a cluster of about six molecules (according to the HSP comparison, at least). There may also be other possibilities. The use of the HSP for water found from the correlation of total water solubility appears to be the most promising set of values to work with at the present time. This is especially true for water in lower energy systems.

It is not yet advisable to include water in a standard set of test liquids for experimental evaluation of the HSP for polymers or other materials because of its tendency to be an outlier. This means a challenge still exists to understand how to be able to incorporate water into a standard set of HSP test liquids without always being concerned about special interpretations for water, and only for water. An example of how this can lead to oddities is discussed in the following.

A characterization problem caused by nonideal mixtures with water is the interpretation of HSP correlations for materials such as the dye Rhodamin FB (C.I. Basic Violet 10).[2,16] Use of mixtures of solvent and water as test solvents led to a very nonspherical (noncircular) cohesion

TABLE 18.5
Calculated Solubility Sphere for Rhodamin FB

Solvent	δ_D	δ_P	δ_H	Solubility	RED	V
Acetone	15.5	10.4	7.0	0	1.125	74.0
Benzene	18.4	0.0	2.0	0	1.991	89.4
1-Butanol	16.0	5.7	15.8	0*	0.999	91.5
Butyl acetate	15.8	3.7	6.3	0	1.517	132.5
gamma-Butyrolactone	19.0	16.6	7.4	0*	0.988	76.8
Cyclohexane	16.8	0.0	0.2	0	2.076	108.7
Diacetone alcohol	15.8	8.2	10.8	1*	1.001	124.2
Diethylene glycol	16.6	12.0	20.7	1	0.486	94.9
Diethylene glycol monomethyl ether	16.2	7.8	12.6	1	0.934	118.0
Diethylenetriamine	16.7	13.3	14.3	1	0.487	108.0
Dimethyl formamide	17.4	13.7	11.3	1	0.677	77.0
Dimethyl sulfoxide	18.4	16.4	10.2	1	0.741	71.3
Dipropylene glycol	16.5	10.6	17.7	1	0.570	130.9
Ethanol	15.8	8.8	19.4	1	0.732	58.5
Ethylene glycol	17.0	11.0	26.0	1	0.815	55.8
Ethylene glycol monoethyl ether	16.2	9.2	16.4	1	0.707	79.1
2-Ethyl hexanol	15.9	3.3	11.8	0	1.294	156.6
Glycerol	17.4	12.1	29.3	1	0.996	73.3
Methanol	15.1	12.3	22.3	1	0.589	40.7
Methylisoamyl ketone	16.0	5.7	4.1	0	1.530	142.8
Methyl-2-pyrrolidone	18.0	12.3	7.2	1*	1.042	96.5
1-Pentanol	15.9	4.5	13.9	0	1.138	108.6
1-Propanol	16.0	6.8	17.4	0*	0.889	75.2
Propylene glycol	16.8	9.4	23.3	1	0.772	73.6
Tetrahydrofuran	16.8	5.7	8.0	0	1.295	81.7
Toluene	18.0	1.4	2.0	0	1.902	106.8
Trichloroethylene	18.0	3.1	5.3	0	1.615	90.2
Water	15.5	16.0	42.3	0	1.965	18.0

Note: δ_D = 16.7; δ_P = 17.5; δ_H = 18.5; Ro = 12.2; FIT = 0.930; NO = 28.

Source: Riedel, G., *Farbe and Lack*, 82(4), 281–287, 1976; Birdi, K.-S., Ed., *Handbook of Surface and Colloid Chemistry*, CRC Press, Boca Raton, FL, 1997, chap. 10.

energy parameter plot (see Figure 18.1). The irregular plot can presumably still be used as such, but the characterization of the dye in question is not useful in relation to prediction of interactions with other materials. The plot has given several individuals the impression that there are significant problems with the HSP approach when it is applied to this kind of material. This is not true. A computer analysis based on the pure solvent data given by Riedel[16] confirms that a good "spherical" characterization of Rhodamin FB is possible using the same data otherwise used in Figure 18.1.[5] The HSP data for this correlation are given in Table 18.5. The data fit was 0.93 for 28 data points. Figure 18.1 clearly shows that this HSP sphere covers more space than the data, with a significant portion in the high energy region where there are no liquids. Chapter 1, Equation 1.9 (with the constant 4) was used in this correlation, as it has been used in all the other HSP correlations in this book. The HSP correlations for water-soluble polymers and other high energy materials involved similar extrapolations into domains where there are no liquids. This procedure may be subject to revision at some future point in time, but for the present it seems to be the only procedure possible to maintain consistency in the HSP procedures developed. It should be remembered that many
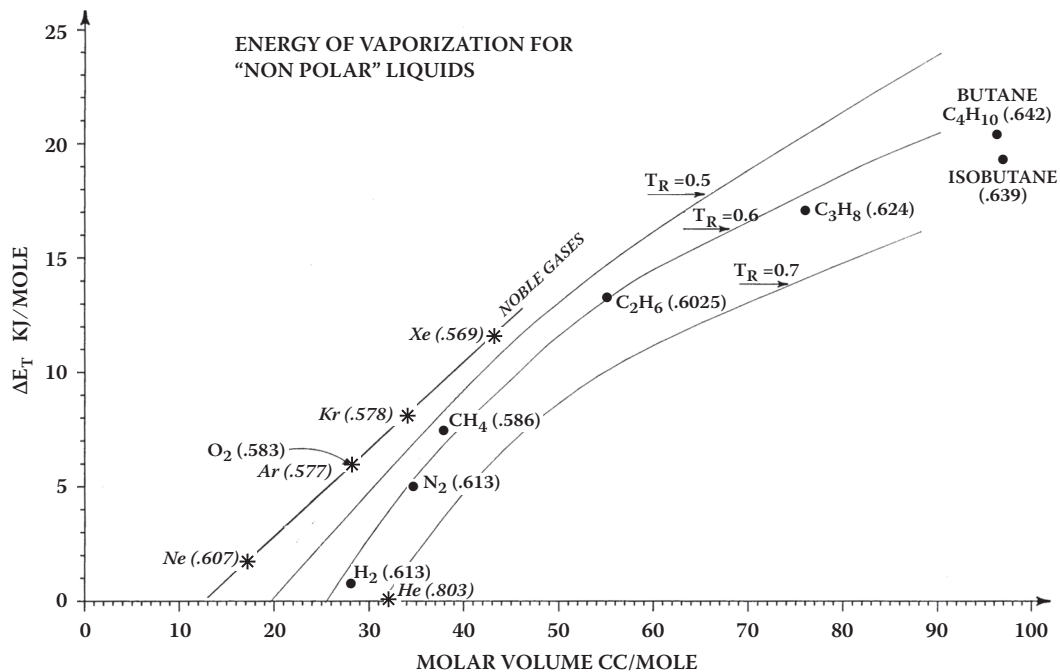
FIGURE 18.2 Cohesion energy for various low molecular weight materials as a function of molecular volume and reduced temperature (given by curves or in parentheses). (See text for discussion.)

(most) liquids with high HSP (water, methanol, glycols) also have low molecular volumes (V). This makes them "better" solvents than expected by comparison with all the other solvents (whose average V is closer to 100 cc/mol). This fact might give the impression that the constant 4 in Chapter 1, Equation 1.9 should be increased. This is discussed more in Chapter 2.

A unifying concept and procedure for the use of water in all testing is needed. The HSP considerations discussed in this book provide help toward reaching this goal.

GASES

HSP can also be used to improve understanding of the solubility behavior of gases. Solubility parameters are usually derived from data at the normal boiling points. HSP derived from these numbers seem to be in good qualitative agreement with expectations (even at 25°C), and in many cases quantitative agreement with physical behavior has also been found. Some examples are given by Barton.[2] Solubility parameter correlations for oxygen[28] (Chapter 13) and nitrogen [29] (Chapter 13) have been used as examples in this book. The δ_P and δ_H parameters for these two gases are zero. HSP for many gases where this is not true are reported in Chapter 13, Table 13.4. A specific example where this is not the case is carbon dioxide. Carbon dioxide is extensively discussed in Chapter 10 where the HSP are calculated for large variations in pressure and temperature. This same procedure is applicable to other gases. Chapter 3 also treats a method to calculate the three partial solubility parameters for gases.

In the process of calculating the HSP for gases, it was found necessary to extrapolate the data in Chapter 1, Figure 1.1 to lower molar volumes. Figure 18.2 is derived from this. This figure is worthy of some consideration from a theoretical point of view. The basis of the HSP is a corresponding states calculation for E_D as the energy of vaporization of a corresponding hydrocarbon solvent (same V and structure) at the same reduced temperature. This is, of course, 298.15 K divided

by the solvent's critical temperature. The reduced temperature at the boiling point is indicated in parentheses in Figure 18.2. Questions can be raised as to why the noble gases differ from the hydrocarbon solvents and whether the hydrocarbon solvents were the best choice as reference materials. Also, why is oxygen among the noble gases in cohesion behavior rather than rated with the other gases? At the time of choice for a reference for the dispersion bonding energies, there were ample data on latent heats for the hydrocarbons and the aliphatic hydrocarbons were considered as having δ_P and δ_H values equal to zero. This may not quite be true, but the corrections would be minor, and the necessary data for a revised reference are lacking. It appears that the currently chartered course of using hydrocarbon solvents as a basis will be maintained. Some additional considerations may be found in further study of the relation of HSP to the corresponding states theory of Prigogine and coworkers as discussed in Chapter 2. The behavior of the hydrocarbon solvents appears to be included within the Prigogine parameter for differences in size (ρ).

ORGANIC SALTS

The HSP of several organic salts have been compared with the HSP for the organic acids and organic bases from which they were made.[30] The result was that the organic salts always had considerably higher HSP than either of the components making them up. As examples, the salts made from formic acid and acetic acid combined individually with dimethyl ethanolamine had $\delta_D;\delta_P;\delta_H$ equal to 17.2;21.5;22.5 and 16.8;19.8;19.8, respectively, whereas the $\delta_D;\delta_P;\delta_H$ are 14.3;11.9;16.6 for formic acid, 14.5;8.0;13.5 for acetic acid, and 16.1;9.2;15.3 for dimethyl ethanolamine. All of these values are in MPa$^{1/2}$. This general relationship was also found for other salts formed by combinations of organic acids with a variety of amines. These values are reported in Appendix Table A.1 in dark type, as there are experimental data to justify the numbers. The HSP for the salts are generally close to those mentioned earlier. These values are high enough to make the salt entities insoluble in most polymers. Their affinities for water will be very high, however, both because of high HSP and also because of the charges associated with the salt groups. There was about 10% shrinkage in volume compared with the original volumes of the acids and bases. In some cases, the cohesion energy of the salts is high enough to make them solids rather than liquids. This study showed that organic salts can indeed be characterized by HSP. More work is necessary, however, with other types of salts. In particular, the acid groups found in nature, such as in hemicelluloses, deserve more attention (see Chapter 15 and Reference 24).

INORGANIC SALTS

The solubility of magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_2O$] was evaluated in a standard set of solvents[1] and later correlated more precisely with HSP. The HSP derived from this are $\delta_D;\delta_P;\delta_H$, and Ro equal to 19.5;22.1;21.9, and 13.2, respectively, all in MPa$^{1/2}$. Nitrates are known to be among the most soluble of salts. Somewhat less soluble than the nitrates are chlorides. These are only partly soluble in a few organic liquids with very high HSP. Group contributions to the HSP from the nitrate group are expected to result in lower HSP, and, in particular, lower δ_D for the nitrate portion of a salt than would be expected from the group contributions from a chloride. This would lead to greater solubility of the nitrates in organic solvents, which is indeed the case. The δ_D parameter seems to be qualitatively capable of describing the behavior of metals to some extent. It may be possible to arrive at an approximate description of inorganic salt solubility in organic media (perhaps water, too) using HSP or some modification/extension thereof. The salting in and salting out of various polymers can perhaps provide clues to assign HSP in this connection. Finally, it should be noted that an excellent HSP correlation of the chemical resistance of an inorganic zinc silicate coating is reported in Chapter 12, Table 12.1.
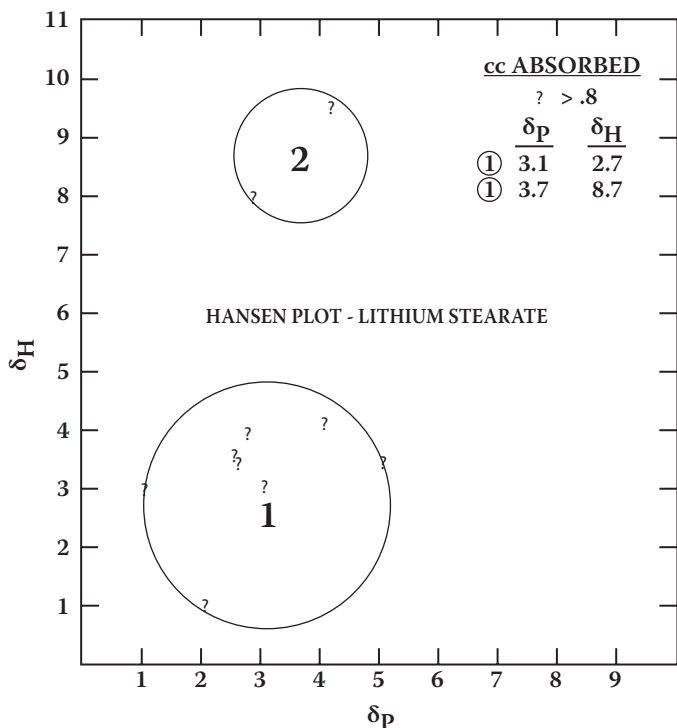
FIGURE 18.3 HSP plot for solvent uptake by lithium stearate.[31,32] Units for δ_P and δ_H are $(cal/cm^3)^{1/2}$. (From Alan Beerbower, personal communication.)

ORGANOMETALLIC COMPOUNDS

No systematic studies of the HSP of organometallic compounds have been made. An exception is perhaps that shown in Figure 18.3 where Beerbower[31] used data from Panzer[32] to show that lithium stearate does indeed have two distinct regions of solvent uptake and that a HSP plot can show why. This example shows that one can calculate HSP values where the relevant data can be found in the literature and then test these with relevant experiments. Group contributions would be valuable. Metallic bonds differ in nature from those usually discussed in connection with organic compounds. A suspicion is that, at least in practice, the cohesion energy derived from the "metallic" bonding in organometallic compounds can be coupled with the dispersion parameter. There is also a question, for example, of whether metal atoms in the center of more complicated molecules are effectively shielded from any (surface) contact with a solvent. Surface contacts are clearly important, but it appears that the nature of the central atom also has an effect. Finally, it might be noted that Hildebrand and Scott presented a chapter on the solubility parameters of metals.[33] Unfortunately, we do not often deal with pure metals in this context, but rather metal oxides, for which no HSP work has been reported, as least not to the author's knowledge.

AROMAS AND FRAGRANCES

Aromas and fragrances are important in connection with packaging materials, foodstuffs, cosmetics, chewing gum, etc. A recent report[34] discussed HSP in connection with fragrances and aromas. It is clear that HSP exist for these materials, but very little work has been published in the area. One of the examples included in Reference 34 was the development of an artificial nose based on coated oscillating sensors, which oscillate more slowly when they gain weight. Matching HSP for the coating and material to be detected leads to increased weight gain and increased sensitivity. Other

examples where HSP could be systematically used include: counteracting undesirable odors using fragrances that have reasonably similar HSP; absorption of odors into plastics, coatings, sealants, etc.; development of packaging with designed HSP to either function as a barrier or as a sink; and an estimate of where a given aromatic material is likely to reside. The key to interpretation is, as usual, that similarity of HSP means higher affinity. It is thought that the masking effect is the result of adsorption of the fragrance on the regions of the sensory system where HSP are similar to those of the undesired odor. There may not be a complete match regarding steric adsorption, but the sensitive areas are covered anyway, and this barrier prevents the odor from arriving at the given sites.

ABSORPTION OF CHEMICALS IN PLASTICS

HSP correlations exist for chemical resistance, permeation phenomena, and uptake of solvents in many polymers. The recycling of polymeric containers has a potential problem in that the polymers used are able to readily absorb those chemicals whose HSP are not too different from their own. Once a chemical has absorbed into a polymer, and particularly if it is a rigid polymer with a relatively high glass transition temperature, it can be very difficult to get it out again. A relatively slow diffusion process is required to do this. See Chapter 16. It is suggested that an extensive HSP analysis be done for those polymers where potential misuse or contamination of containers prior to recycling is a possibility. This can point out which chemicals are most likely to present the greatest problems.

CHEMICAL RESISTANCE

Chemical resistance studies have generally been performed with too few liquids and without the necessary spread of HSP to allow the data to be correlated with confidence. In addition, attainment of equilibrium is not usually confirmed. These shortcomings mean that HSP correlations of chemical resistance must be done with great care. This has been discussed in Chapter 12 in more detail. An additional activity, which should be done for practical reasons, is to assign effective HSP to various test materials such as mustard, ketchup, and other given products that often appear in tests of chemical resistance. Such data will allow greater use of the correlations since guidelines for potential improvements can be obtained.

CONTROLLED RELEASE

HSP considerations can provide an extra formulating parameter for the controlled release of drugs. When the HSP relations between a drug and its surroundings are known, predictions of its behavior can be made. When there is a good match in the HSP values, the drug will be more soluble with the ability to move at some rate within a polymer matrix. On the other hand it can be surrounded by a matrix with similar HSP, and this may slow release more than desired. A poor match in HSP may leave holes and expose the drug for more rapid release. When the match is poor, the drug will not be able to permeate through its polymeric surroundings, but it can, of course, pass through open passageways. Drugs will also tend to adsorb at surfaces where there is a good HSP match.

It has been shown (personal communication, Andreas Gryczke, Degussa Pharma Polymers, Darmstadt) that calculations of HSP for a number of drugs and for a series of EUDRAGIT® polymers provided a correlation confirming that the drugs are soluble in those polymers where the HSP match closely enough. When the drug and polymer HSP were within 10 MPa$^{1/2}$ at the concentration studied (20% wgt.), what appeared to be true solubility was found. This was evidenced by x-ray diffraction and DSC measurement that confirmed the drugs were embedded completely amorphous (solid solution). A closer match would presumably be required to do this for higher concentrations of the drugs.

Table 18.6 contains HSP for some materials whose solubility in various media may have interest. It is possible to calculate HSP for essentially all drugs, although hydrochlorides and other salts

TABLE 18.6
Calculated HSP for Various Materials

Material	δ_D	δ_P	δ_H	V
Adrenaline	20.5	8.7	19.9	154.5
4-Aminopyridine	20.4	16.1	12.9	87.1
Ascorbic Acid	18.0	12.6	27.6	106.7
Caffeine	19.5	10.1	13.0	157.9
Cycloheximide	18.3	11.0	13.8	171.0
DDT	20.0	5.5	3.1	268.8
Dopamine	18.2	10.3	19.5	180.0
Ecstacy	18.0	5.1	6.1	202.9
Meclofenoxate (base only)	16.0	6.2	9.0	198.3
Norephedrin	18.0	10.7	24.1	141.9
2-Oxopyrrolidinacetamid	17.5	15.6	11.2	116.2
Quinine	19.0	4.6	11.0	310.7
Saccharin	21.0	13.9	8.8	206.8
Serotonin	18.0	8.2	14.4	144.4
Spermidin	16.7	11.2	12.0	155.6

Note: Units are MPa$^{1/2}$.

Source: Hansen, C.M., *Conference Proceedings, Pharmaceutical and Medical Packaging 2001*, Skov, H. R., Ed., Hexagon Holding, Copenhagen, 2001, pp. 20.1–20.10.

should be measured rather than calculated only, as there is very little experimental data on which to base an estimate with group contributions.

There are correlations of HSP with skin permeation presented in Chapter 15 that should allow an estimate of which drugs can enter via this route. Simple calculations confirm that dopamine, nicotine, skatole, and nitroglycerine, for example, have high affinity for skin.

NANOTECHNOLOGY

Controlling the orientation of molecules can be a key for switches and the like. An example has been given in Chapter 15 where anthracene units appended to a polymer molecule adopted one orientation in toluene at room temperature, but changed to a new orientation at temperatures above 38.5° in toluene. The configuration at the higher temperatures was also that adopted in tetrahydrofurane. This change of orientation is the result of a poorer solvent at the higher temperatures compared with a good one at room temperature. More details and additional examples are found in Chapter 15.

The following link reports what follows for studies of organically modified nanoclays (organoclay) in nanocomposites:

http://www.hwi.buffalo.edu/ACA/ACA03/abstracts/text/W0383.html

Quote:

W0383

Evaluating Organoclays for Nanocomposites by Small Angle Scattering. Derek L. Ho[1,2] and Charles J. Glinka[1], [1]Center for Neutron Research, National Institute of Standards and Technology,

Gaithersburg, MD 20899, [2]Dept. of Materials and Nuclear Engineering, Univ. of Maryland, College Park, MD 20742.

Understanding the interaction between organically modified clay (organoclay) platelets and organic solvent molecules as well as the corresponding structure of organoclays in a suspension is a critical step toward tailoring and characterizing nanocomposites formed by organoclays in a polymer matrix. Recently, nanocomposites composed of clays and polymers have been found to have improved mechanical properties as well as enhanced thermal stability. The improved properties are related to the degree of dispersal and exfoliation of the clay platelets in the polymer matrix. In order to understand and optimize potential processing conditions, organoclays were dispersed in a number of organic solvents covering a range of solubility parameters and characterized using small-angle neutron scattering and wide-angle x-ray scattering techniques. With Hansen's solubility parameters, $\delta_o^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$, the correlation between the degree of exfoliation of organoclays and the solvent in which the clay platelets are dispersed/mixed has been analyzed. It has been found that the dispersion force of the solvent, reflected by δ_d, is the principal factor determining whether the clay platelets remain suspended in the solvent while the polar (δ_p) and hydrogen-bonding (δ_h) forces affect primarily the tactoid formation/structure of the suspended platelets. The organically modified clays studied in this work precipitated in any solvent with molecules with moderately strong hydrogen-bonding groups. The correlation found has been used to correctly identify a solvent, trichloroethylene, which completely exfoliates the organoclays studied in this work.

These and the many other examples in this handbook related to self-assembly (see above), surface adsorption, molecular orientation, and affinity among molecules and molecular segments should provide ample evidence that molecular guidance in nanotechnology endeavors can be found in the HSP concept.

THEORETICAL PROBLEMS AWAITING FUTURE RESOLUTION

POLYMER SOLUBILITY

The Flory chi parameter has been used to describe polymer–solvent interactions for many years.[35,36] If this single parameter is to be complete in this function, it must include both the atomic/dispersion interactions as well as the specific interactions reflected by the δ_P and δ_H parameters. Attempts to calculate chi using HSP are reported in Chapter 2. More understanding is required before chi can be calculated with reasonable accuracy, but intensified efforts seem warranted. Zellers and coworkers have recently made an attempt to use this theory in conjunction with HSP studies.[37–40] A major problem is the reliability of the chi parameter (and also HSP) values in the literature (see Chapter 2 for more details). Chapter 4 is a lengthy discussion of the use of HSP in thermodynamic models for polymer solutions.

The author's current view as expressed in Chapter 2 is that the Flory approach is a special case of the more general Prigogine corresponding states theory. This is in agreement with the view of Patterson discussed in Chapter 2. Furthermore, the very general applications of the HSP approach demonstrated in this book and elsewhere, and the apparent agreement in the treatment of specific interactions by both the HSP and Prigogine treatments, leads to confidence in the HSP approach. The geometric mean must be used in the Prigogine theory to arrive at this similarity of treatment. The statistical thermodynamic approach of Panayiotou and coworkers thoroughly discussed in Chapter 3 provides convincing evidence that the division of the cohesion energy density into three parts (at least) is the correct procedure to understand affinities among many types of materials. Finally, Chapter 4 deals with theories of vapor–liquid equilibrium in particular and how these relate to HSP.

SURFACE PHENOMENA

Surfaces can clearly be characterized by HSP as demonstrated in Chapter 6 and Chapter 7. The work of Beerbower contained in Reference 17 and Reference 23 has also shown applications of HSP to such varied phenomena as the work of adhesion of liquids on mercury, friction of polyethylene untreated and treated with sulfuric acid, the Rehbinder effect — the crushing of aluminum oxide (Al_2O_3) under various liquids, and the Joffé effect — effect of liquid immersion on the fracture strength of soda-lime glass. Here again, the successful use of HSP to such applications might not have been anticipated had it been considered as a parameter for use in bulk systems only. A formalized unifying theory linking HSP to both bulk and surface phenomena is still lacking. Presently, the best that can be said is that the generality "like dissolves like" can be quantified in many cases. The extension of this, "like seeks like," also seems to have been demonstrated. It is the surfaces of molecules which interact with each other (also in bulk and solution phenomena), so it is not surprising that cohesion parameters can be applied with success to both solubility and surface phenomena. Much more research needs to be done with these relations. A good starting point is the *Handbook of Surface and Colloid Chemistry*, edited by K.S. Birdi.[41] If we consider chromatographic techniques as depending primarily on surface phenomena, mention should also be made of the extension of the three-parameter HSP approach to a five-parameter approach by Karger and coworkers.[42] HSP characterizations of surfactants are also badly needed.

CONCLUSION

HSP have been shown useful in solvent selection; predicting polymer–polymer miscibility; characterizing the surfaces of polymers, fillers, and fibers; correlating permeation phenomena; characterizing organic salts and inorganic salts; gas solubility; etc. No other parameter can be assigned to such a range of materials spanning from gases and liquids, over surfaces, to inorganic salts. These results and the close relation with the Prigogine corresponding states theory of polymer solutions, and more recently to the work of Panayiotou summarized in Chapter 3, indicate that a still more general theory exists. This theory should quantify the adage "like seeks like," i.e., include surface phenomena as well as bulk phenomena.

Specific areas needing more theoretical work related to HSP in the near future include better understanding of usage for predictions of behavior for water, gases, organic salts, inorganic salts, and organometallic compounds. Water remains special because of its low molecular volume and high δ_H. Most materials having HSP in the range of the customary test liquids can be studied using HSP with reasonable success. This is not fully the case for gases, many of which have much lower HSP than the well-studied liquids, and salts, many of which apparently have HSP very much higher than any of the liquids. Extensions of practical applications related to chemical resistance and the uptake of potentially dangerous materials in polymers are also required. Finally there is a great deal to be done in the areas of controlled drug release, improved understanding of some biological processes, and last but not least, the systematic use of HSP in nanotechnology to control the assembly and orientation of molecules or segments of molecules.

REFERENCES

1. Hansen, C.M., The universality of the solubility parameter, *Ind. Eng. Chem. Prod. Res. Dev.*, 8(1), 2–11, 1969.
2. Barton, A.F.M., *Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Boca Raton, FL, 1983; 2nd ed., 1991.
3. Barton, A.F.M., *Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters*, CRC Press, Boca Raton, FL, 1990.

4. Hansen, C.M., Solubility parameters, in *Paint Testing Manual*, Manual 17, Koleske, J.V., Ed., American Society for Testing and Materials, Philadelphia, PA, 1995, pp. 383–404.

5. Hansen, C.M., Cohesion energy parameters applied to surface phenomena, *CRC Handbook on Surface Science*, Birdi, K.S., Ed., CRC Press, Boca Raton, FL, 1997, chap. 10.

6. Anonymous, Brochure: Co-Act — A Dynamic Program for Solvent Selection, Exxon Chemical International Inc., 1989.

7. Dante, M.F., Bittar, A.D., and Caillault, J.J., Program calculates solvent properties and solubility parameters, *Mod. Paint Coat.*, 79(9), 46–51, 1989.

8. Hansen, C.M. and Beerbower, A., Solubility parameters, in *Kirk-Othmer Encyclopedia of Chemical Technology,* Suppl. Vol., 2nd ed., Standen, A., Ed., Interscience, New York, 1971, pp. 889–910.

9. Hansen, C.M. and Andersen, B.H., The affinities of organic solvents in biological systems, *J. Am. Ind. Hyg. Assoc.*, 49(6), 301–308, 1988.

10. Wessling, R.A., The solubility of poly(vinylidene chloride), *J. Appl. Polym. Sci.*, 14, 1531–1545, 1970.

11. Grulke, E.A., Solubility parameter values, in *Polymer Handbook*, 3rd ed., Brandrup, J. and Immergut, E.H., Eds., John Wiley-Interscience, New York, 1989, pp. VII/519–559.

12. Burrell, H., Solubility of polymers, in *Kirk Othmer Encyopedia of Polymer Science and Technology*, Vol. 12, 2nd ed., John Wiley & Sons, New York, 1970, pp. 618–626.

13. Hoy, K.L., New values of the solubility parameters from vapor pressure data, *J. Paint Technol.*, 42(541), 76–118, 1970.

14. Hoy, K.L., *Tables of Solubility Parameters*, Union Carbide Corp., Research and Development Dept., South Charleston, WV, 1985; 1st ed. 1969.

15. van Krevelen, D.W. and Hoftyzer, P.J., *Properties of Polymers: Their Estimation and Correlation with Chemical Structure,* 2nd ed., Elsevier, Amsterdam, 1976.

16. Riedel, G., The solubility of colorants in organic solvents (Löslichkeit von Farbstoffen in organischen Lösungsmitteln, in German), *Farbe und Lack*, 82(4), 281–287, 1976.

17. Beerbower, A., Environmental capability of liquids, in *Interdisciplinary Approach to Liquid Lubricant Technology*, NASA Publication SP-318, 1973, 365–431.

18. Fedors, R.F., A method for estimating both the solubility parameters and molar volumes of liquids, *Polym. Eng. Sci.*, 14(2), 147–154, 472, 1974.

19. Koenhen, D.N. and Smolders, C.A., The determination of solubility parameters of solvents and polymers by means of correlation with other physical quantities, *J. Appl. Polym. Sci.*, 19, 1163–1179, 1975.

20. Utracki, L., Personal communication, 1995.

21. Kähler, T. and Knudsen, S.L., Student Report, Technical University of Denmark, 1967.

22. Hansen, C.M., Characterization of surfaces by spreading liquids, *J. Paint Technol.*, 42(550), 660–664, 1970.

23. Beerbower, A., Boundary Lubrication — Scientific and Technical Applications Forecast, AD747336, Office of the Chief of Research and Development, Department of the Army, Washington, D.C., 1972.

24. Hansen, C.M. and Björkman, A., The ultrastructure of wood from a solubility parameter point of view, *Holzforschung*, 52(4), 335–344, 1998.

25. Hansen, C.M. and Knudtson, J., Spreading and wetting of an electrodeposition coating (Ausbreitung und Benetzung bei einem Elektrotauchlack, in German), *Farbe und Lack*, 2, 115–118, 1973.

26. *Progress in Organic Coatings*, Special issue devoted to Self-Stratifying Coatings, 28(3), July 1996.

27. Thulstrup, D., Characterization of surfaces by static contact angle measurements (lecture in Danish: Karakterisering af Overflader ved Statisk Kontaktvinkelmåling), Surface Properties and Modification of Plastics (Conference Notes), Ingeniørforening i Danmark, November 13, 1997, Copenhagen. See also DSM Materialenyt 2:97, Dansk Selskab for Materialeproevning og -forskning, Ingeniørforening in Danmark, Copenhagen, 1997, 63–69.

28. König, U. and Schuch, H., Molecular composition and permeability of plastics, (Konstitution und Permeabilität von Kunststoffen, in German), *Kunststoffe*, 67(1), 27–31, 1977.

29. Hansen, C.M., 25 years with solubility parameters (25 År med Opløselighedsparametrene, in Danish), *Dan. Kemi*, 73(8), 18–22, 1992.

30. Hansen, C.M., Some aspects of acid/base interactions (Einige Aspekte der Säure/Base-Wechselwirkung, in German), *Farbe und Lack*, 83(7), 595–598, 1977.

31. Beerbower, A., Personal communication, Predicting Wetting in the Oil-Brine-Rock System, Unedited manuscript for presentation at the National AIChE Meeting, Tulsa, OK, March 10–13, 1974.

32. Panzer, J., Components of solid surface free energy from wetting measurements, *J. Colloid Interface Sci.*, 44(1), 142–161, July 1973.

33. Hildebrand, J. and Scott, R.L., *The Solubility of Nonelectrolytes*, 3rd ed., Reinhold, New York, 1950.

34. Hansen, C.M., Solubility parameters for aromas and scents (Aromastoffers Opløselighedsparametre, in Danish), *Plus Process*, 11(9), 16–17, 1997.

35. Flory, P.J., *Principles of Polymer Chemistry*, Cornell University Press, New York, 1953.

36. Eichinger, B.E. and Flory, P.J., Thermodynamics of polymer solutions, *Trans. Faraday Soc.*, 64(1), 2035–2052, 1968; 64(2), 2053–2060, 1968; 64(3), 2061–2065, 1968; 64(4), 2066–2072, 1968.

37. Zellers, E.T., Three-dimensional solubility parameters and chemical protective clothing permeation. I. Modelling the solubility of organic solvents in Viton® gloves, *J. Appl. Polym. Sci.*, 50, 513–530, 1993.

38. Zellers, E.T., Three-dimensional solubility parameters and chemical protective clothing. II. Modelling diffusion coefficients, breakthrough times, and steady-state permeation rates of organic solvents in Viton® gloves, *J. Appl. Polym. Sci.*, 50, 531–540, 1993.

39. Zellers, E.T., Anna, D.H., Sulewski, R., and Wei, X., Critical analysis of the graphical determination of Hansen's solubility parameters for lightly crosslinked polymers, *J. Appl. Polym. Sci.*, 62, 2069–2080, 1996.

40. Zellers, E.T., Anna, D.H., Sulewski, R., and Wei, X., Improved methods for the determination of Hansen's solubility parameters and the estimation of solvent uptake for lightly crosslinked polymers, *J. Appl. Polym. Sci.*, 62, 2081–2096, 1996.

41. Birdi, K.S., *Handbook of Surface and Colloid Chemistry*, CRC Press, Boca Raton, FL, 1997.

42. Karger, B.L., Snyder, L.R., and Eon, C., Expanded solubility parameter treatment for classification and use of chromatographic solvents and adsorbents, *Anal. Chem.*, 50(14), 2126–2136, 1978.