

## Applications of solubility parameters and other cohesion parameters in polymer science and technology

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**Abstract** - Cohesion parameters (solubility parameters) provide one of the simplest methods of correlating and predicting the cohesive and adhesive properties of polymers and solvents from a knowledge of the properties of the individual components alone. It is therefore not surprising that there are severe limitations on their precision. Whether or not any correlation or prediction is "satisfactory" depends on the precision that is expected or needed. When one is looking for relatively minor differences in behaviour, such as solubility differences between isomeric liquids or between polymers with different degrees of cross-linking, cohesion parameters may not be appropriate. The most important situation where caution is required in using Hildebrand parameters or Hansen parameters is where the extent of donor-acceptor (Lewis acid-Lewis base) interactions (particularly hydrogen bonding) within a component is very different from that between components.

There is a group of parameters of dimension (pressure)<sup>1/2</sup> which are concerned with the cohesive properties of materials, and the term cohesion parameter is a good general description (ref. 1,2). The original solubility parameter defined by J.H. Hildebrand and R.L. Scott (ref. 3)

$$\delta = [(\Delta G_H - RT)/V]^{1/2}$$

is now most appropriately called the Hildebrand parameter, and the widely used subdivision into dispersion (d), polar (p) and hydrogen bonding (h) components by C.M. Hansen (ref. 4) gave rise to Hansen parameters,  $\delta_d$ ,  $\delta_p$ ,  $\delta_h$ .

The significance of the term "cohesion" and the dimension (pressure)<sup>1/2</sup> are clear when one considers that when mixing of *i* and *j* occurs, the change in cohesive energy density or cohesive pressure (*c*) is given by the exchange energy density or interchange cohesive pressure, *A*:

$$ij_A = i_c + j_c - 2ij_c$$

(Two *i*-*j* interactions are formed for each pair of *i* and *j* interactions broken.) Thus, using the geometric mean approximation for  $ij_c$ ,

$$ij_c = (i_c j_c)^{1/2},$$

$$ij_A = (i_c^{1/2} - j_c^{1/2})^2 = (i_\delta - j_\delta)^2$$

In terms of Hansen parameters,

$$ij_A = (i_{\delta_d} - j_{\delta_d})^2 + (i_{\delta_p} - j_{\delta_p})^2 + (i_{\delta_h} - j_{\delta_h})^2.$$

It is obvious from this expression that it is convenient to define a sphere of solubility, centre ( $j_{\delta_d}$ ,  $j_{\delta_p}$ ,  $j_{\delta_h}$ ), and to compare the distance  $ij_A^{1/2}$  of any solvent *i* from the centre with the radius of that sphere.

The most convenient unit for cohesion parameters is MPa<sup>1/2</sup>, numerically equal to J<sup>1/2</sup> cm<sup>-3/2</sup> and MJ<sup>1/2</sup> m<sup>-3/2</sup>, and

$$1 \text{ cal}^{1/2} \text{ cm}^{-3/2} = 2.0455 \text{ J}^{1/2} \text{ cm}^{-3/2}$$

Cohesion parameters provide one of the simplest methods of correlating and predicting the cohesive and adhesive properties of materials from a knowledge of the properties of the

individual components. It is therefore to be expected that there will be severe limitations on their use. This paper is concerned with examples of situations where cohesion parameters do not work very well. In fact, what is surprising is that this method works as well as it does: it is really a semi-quantitative version of the statement "like dissolves like".

For liquids, it is possible to evaluate the Hildebrand parameter directly and exactly from the experimentally accessible vaporisation enthalpy and molar volume according to its definition. It was originally applied only to regular solutions (those with a zero partial excess entropy) and it is most useful for those liquids and systems which are approximately regular. Nevertheless, the Hildebrand parameter may be evaluated directly from experimental data for all liquids. Rather, the relationships derived from this defining equation involve approximations.

For gases and solids, it is quite reasonable to extrapolate downwards or upwards in temperature in order to evaluate liquid-like cohesion parameters: one is then considering a hypothetical superheated or subcooled liquid rather than a gas or solid. It should be emphasized that use of the vaporization or sublimation enthalpy of a solid, less the expansion work  $RT$ , but uncorrected for the crystal-liquid transition does not yield a Hildebrand parameter. It does provide a useful cohesion parameter, but not a Hildebrand parameter. The need for distinctions such as this is the justification for introducing carefully thought-out terms rather than the less specific "solubility parameter".

For polymers, it is not usually possible to obtain the vaporisation enthalpy directly, so there is really no alternative to the empirical determination of quantities which give the best over-all description of various properties: solubility, swelling, polymer-polymer and polymer-liquid compatibility. Even without the introduction of crystallinity factors, although polymers may be liquid-like, they are not liquids, so the cohesion parameter concept must be approached differently. Even if one uses group molar attraction constants to evaluate cohesion parameters, there is no reason to assume that the "best" values of the constants to use are those based on results of liquid systems.

If polymers are crystalline, they tend to be insoluble in most solvents. This is explained in cohesion parameter terms by saying that there is an additive enthalpy term associated with fusion or disordering. Only if there are strong, specific interactions such as hydrogen bonding can this additional crystal stability term be overcome so that dissolution can take place. Examples are the dissolution of cellulose in 70% sulfuric acid and the dissolution of nylon in phenol.

From the Hildebrand parameter concept, the original definition for regular solutions, one can go on to derive the Hildebrand-Scatchard equation and expressions for activity coefficients and related quantities. The cohesion parameters can be subdivided into contributions from various types of molecular interactions. In all cases, however, some approximations or assumptions are made, and the expressions are not exact even for liquids, let alone polymers. They are best considered as useful, empirical expressions which have some theoretical foundation but which are chosen for their practical usefulness in particular situations. It should be noted that whether or not any particular correlation or prediction method is considered to "work" depends on the precision that is expected in the application being considered.

The most important situation where caution is required is where donor-acceptor interactions within a component are very different from those between components. Common examples are systems involving hydrogen bonding: alcohols (particularly methanol), carboxylic acids, water, primary and secondary amines, and glycol ethers.

Most commonly, it is hydrogen bonding within the pure component which causes most problems, as one tends to take this for granted, whereas one is more on the alert for new interactions between components.

Although this has long been understood in a general way, it was put most clearly by Hoy (ref. 5), who proposed the term "chameleonic" for those compounds which had the ability to assume the character of the surrounding environment, after the reptile which can take on the colour of its background. By dimerization or intramolecular association what would otherwise be a polar material can behave in a non-polar manner, thus minimising the energy. Examples are dimerization of carboxylic acids, intramolecular association in glycol ethers, alkoxybutanols and diols and formation of tetramers, hexamers or long chains in methanol and methanol-ethanol mixtures. It is clear that the cohesion parameters of associated and dissociated forms of these materials are very different, so the particular values exhibited depends on the situations in which they occur.

In the case of water, for example, it is necessary to distinguish between systems of water with low permittivity organic liquids (i.e. associated water, with limited interaction between water and organic molecules) and systems of water with hydrogen-bonding organic liquids where there is more intermolecular association at the expense of intramolecular association.

In terms of Hansen parameters, the properties of water are described in Table 1.

TABLE 1. Hansen parameters for water

	$\delta_d/\text{MPa}^{1/2}$	$\delta_p/\text{MPa}^{1/2}$	$\delta_h/\text{MPa}^{1/2}$	$\delta_t/\text{MPa}^{1/2}$
self-associated water (water with low permittivity organic liquids)	20	18	18	32
water with hydrogen-bonding organic liquids	12-16	16-31	34-42	48

It is worth emphasizing:

- (i) that the  $\delta_t$  value of pure water is a definite, experimental figure,  $[(\Delta H - RT)/V]^{1/2}$ , but the way it is subdivided into Hansen parameters is less clear;
- (ii) that because  $\delta_t^2 = \delta_h^2 + \delta_d^2 + \delta_p^2$ ,  $\delta_h$  for "hydrogen bonding water" dominates;
- (iii) that although a maximum cohesion capability of  $48\text{MPa}^{1/2}$  exists in water, much of this is unavailable for interaction with low permittivity, non-associating organic liquids which "see" a much lower value.

The mutual solubilities of water with straight-chain alcohols (ref. 6) illustrate the problem. The maximum proportion of alcohol in the aqueous phase falls off rapidly as the chain length increases, decreasing from about 1 mol/L at  $C = 4$  to  $10^{-6}$  mol/L at  $C = 14$ . However, it is not often appreciated that the proportion of water in the alcohol-rich phase remains relatively high, even for long-chain alcohols. A water-alcohol mole ratio of 0.3 is observed for 1-dodecanol, compared with 1.0 for 1-butanol. This can be explained by considering water molecules in the alcohol-rich phase to be locally hydrogen bonded to alcohol groups, even when embedded in a hydrogen matrix, in contrast to the inability of the long-chain alcohols to be accommodated in the extended hydrogen bonded network of water. In this situation, it is clear that one cannot use a single Hildebrand parameter or even a single set of Hansen parameters to describe the behaviour of either water or the long-chain alcohols.

The problem in all such examples is that Hildebrand parameters and Hansen parameters are trying to indicate the values of two or more quantities with one number or one set of numbers:

- (i) the extent of cohesion within the pure compound; and
- (ii) the potential for cohesion in mixtures, in different situations.

When one says that the Hansen hydrogen bonding parameter,  $\delta_h$ , of ethanol is  $20\text{MPa}^{1/2}$ , it means that within pure ethanol  $\delta_h^2$  is the extent of cohesion due to hydrogen bonding, and presumably infers that  $\delta_h$  reflects the hydrogen bonding capability in a mixture. It is clear that this approach works best when the two components of the mixture are similar, and as the difference increases, situations arise where the effective  $\delta_h$  may be much less than or much greater than that in the pure liquid.

As far as hydrogen bonding is concerned, some pure compounds are both proton donors and proton acceptors: here the extent of cohesion due to association in a mixture generally can have any value up to that existing in the pure compound. Examples are alcohols, carboxylic acids, water, and primary and secondary amines.

In contrast, many compounds have a dominant ability to accept protons: ketones, aldehydes, esters, ethers, tertiary amines, aromatic hydrocarbons, alkenes. Here the potential for cohesion in mixtures is greater than that in the pure compound. There are also some proton donors only, such as chloroform.

It is clear that neither Hildebrand parameters nor Hansen parameters are adequate to handle this problem in a quantitative way. There are two methods which can be used:

- (i) treat each associated species in both pure liquids and mixtures as a new compound, with a formation constant and a cohesion parameter value which can be evaluated. This type of approach is fairly traditional and well-established, but rather cumbersome;
- (ii) use a full set of interaction cohesion parameters or specific cohesion parameters,  $\delta_d$ ,  $\delta_i$ ,  $\delta_o$ ,  $\delta_a$ ,  $\delta_b$ , including dispersion, induction, orientation and Lewis acid and base terms (ref. 7). It is this approach which I think has the greatest practical potential.

The net change of cohesive pressure on mixing  $i$  and  $j$  is

$$ij_A = i_c + j_c - 2ij_c$$

(recall that  $i_c = i_{\delta^2}$ ,  $j_c = j_{\delta^2}$  in the original Hildebrand approach). With the subdivision according to specific interactions, the relevant quantities are  $ij_{Ad}$ ,  $ij_{Ao}$ ,  $ij_{Ai}$  and  $ij_{Ab}$ . The first two must be positive:

$$ij_{Ad} = (i_{\delta_d} + j_{\delta_d} - 2i_{\delta_d}j_{\delta_d}) = (i_{\delta_d} - j_{\delta_d})^2$$

$$ij_{Ao} = (i_{\delta_o} - j_{\delta_o})^2$$

The other terms may be positive or negative:

$$ij_{Ai} = 2(i_{\delta_d} - j_{\delta_d})(i_{\delta_i} - j_{\delta_i})$$

$$ij_{Ab} = 2(i_{\delta_a} - j_{\delta_a})(i_{\delta_b} - j_{\delta_b})$$

The total is given by:

$$ij_A = \sum_k ij_{Ak}$$

When  $ij_{Ab}$  is large and negative, exothermic mixing may be explained, in contrast to mixing being restricted to athermic or endothermic processes when only dispersion and polar forces exist.

Thus the answer to the criticism that Hildebrand parameters cannot cope with association or exothermic interactions is that they should be expressed as partial or interaction cohesion parameters. The price to be paid is the greater complexity of evaluation and use.

It will be recalled that polymer Hildebrand parameters cannot be determined directly from the enthalpy of vaporisation. One common method is to determine the effect on the polymer of a series of solvents with gradually increasing Hildebrand parameter values to form a "solvent spectrum". The Hildebrand parameter of the polymer is taken as the mid-point of the range of solvent Hildebrand parameters which provides complete miscibility, or the maximum swelling in the case of a cross-linked polymer which does not dissolve. Normally the solvents are chosen in three categories: weak, moderate or strong hydrogen bonding. The selected solvent is usually added to a 1 or 2g sample of the solid polymer in a test-tube, with an amount of solvent such that the final solution has the correct composition for that polymer in normal use. The mixture may be warmed and stirred to increase the rate of dissolution, but it is cooled and observed at room temperature. By successive choices, upper and lower pairs of two adjacent solvents in the "spectrum" are found, one which dissolves the polymer and one which does not.

Properties related to solubility which may also be used are: the temperature at which the dilute polymer suspension becomes homogeneous; dissolution rate; and peel strength adhesion of polymer films cast from the solvent. More sophisticated methods take into account molar volume differences between polymer and solvent, providing functions which can be plotted to yield straight lines rather than curves with maxima. "Fine control" over solvent Hildebrand parameter values can be provided using mixtures of solvents, the effective Hildebrand parameter of a mixture being calculated on the basis of a volume fraction average. Alternatively, group contribution methods may be used. The molar mass and other properties of the repeating unit can be used to evaluate the Hildebrand parameter of a polymer.

There follow several recently published examples illustrating the limitations of Hildebrand parameters and Hansen parameters in the correlation and prediction of polymer-solvent behaviour.

Perhaps the clearest example of chameleonic behaviour in polymers is where a polymer shows a double peak in the plot of solubility or swelling as a function of the solvent Hildebrand parameter. Thus the polytetrafluoroethylene-styrene-sulfonic acid exchange membrane shows two peaks, the one at lower  $\delta$  values being described as "organic", and that at higher  $\delta$  values as "ionic". Here the acid form of the membrane has two peaks, but the peak at lower Hildebrand parameter values disappears when the membrane is neutralized (ref. 8).

In another example, where this time the polymer is chameleonic, Graham and co-workers (ref. 9) of the University of Strathclyde have illustrated how the swelling behaviour of a poly-(ethylene oxide) hydrogel depends on the type of solvent. If one uses the "maximum swelling" criterion to determine a polymer Hildebrand parameter, the result depends on which class of solvent is used. Plotted on one graph, they would show multiple peaks, but when individual plots for various classes of solvent are made, the result is clearer. In non-hydrogen

bonding solvents (chlorinated, nitrated and unsubstituted hydrocarbons, aldehydes and ketones) the maximum is at about 20 MPa<sup>1/2</sup>, while in esters it is about 22 MPa<sup>1/2</sup> and in alcohols it is at 24 MPa<sup>1/2</sup>. If one had used methanol, formamide and water as swelling agents, the poly(ethylene oxide) would have demonstrated a Hildebrand parameter of about 41 MPa<sup>1/2</sup>.

It is clear that there are extreme limitations on the use of Hildebrand parameters, and to overcome some of these problems, Hansen parameters have been widely used for polymer systems. First, consider what is more-or-less normal behaviour for polymers in mixed solvents, when the composition of the solvent is varied. Both solubility and swelling of Vedril, a poly(methyl methacrylate), in ethanol/water mixtures show a sharp maximum at about 0.8 volume fraction of ethanol (ref. 10). The value of  ${}^i j_A$  (interchange cohesive pressure) calculated from the individual Hansen parameters passes through a minimum at about the same composition. It is found in general that a minimum in  ${}^i j_A$  is generated more frequently if one reduces the weighting of the polar and hydrogen bonding effects by the correction factor  ${}^i j_b$ :

$${}^i j_A = ({}^i \delta_d - j_{\delta_d})^2 + {}^i j_b [({}^i \delta_p - j_{\delta_p})^2 + ({}^i \delta_h - j_{\delta_h})^2]$$

(Here  ${}^i \delta$  is the volume fraction average cohesion parameter of ethanol and water at each composition,  $j_{\delta}$  is the polymer cohesion parameter). Originally this  $b$ -factor was intended to provide a corrective term for induction, but it has the same effect as Hansen's factor of 4 introduced to provide a more spherical grouping of data points:

$${}^i j_A = \frac{{}^i j R^2}{4} = ({}^i \delta_d - j_{\delta_d})^2 + 0.25 [({}^i \delta_p - j_{\delta_p})^2 + ({}^i \delta_h - j_{\delta_h})^2]$$

A value of  ${}^i j_b = 0.2$  gives the best fit for poly(methyl methacrylate)/ethanol/water; if  $b = 1$  no minimum in  ${}^i j_A$  is predicted. The Hansen parameter values used are shown in Table 2.

TABLE 2. Hansen parameter values

	$\delta_d$ /MPa <sup>1/2</sup>	$\delta_p$ /MPa <sup>1/2</sup>	$\delta_h$ /MPa <sup>1/2</sup>
water	19.5	17.8	17.6
ethanol	15.8	8.8	19.4
PMMA	17.8	5.7	7.8

Horta and Fernandez-Pi erola (ref. 11) also studied poly(methyl methacrylate), in terms of cosolvency (where a mixture of two non-solvents is a solvent for the polymer, or where solubility improves when solvents are mixed) and "co nonsolvency" (the reverse: coprecipitation). Cosolvents for PMMA were classified as "symmetric" or "nonsymmetric". Symmetric cosolvents are those where there is one nonsolvent with higher Hildebrand parameter, one with lower Hildebrand parameter, than the polymer: these systems are readily understood in terms of Hildebrand parameters. However the nonsymmetric mixtures, such as acetonitrile with alcohols or formamide with ethanol, cannot be explained in terms of simple Hildebrand parameters as both solvents have  $\delta$  values higher than that of the polymer. The first case can be explained by looking at the Hansen parameters. Acetonitrile occupies a key role:  $\delta_h$  is close to that of the polymer, and  $(\delta_d^2 + \delta_p^2)$  for acetonitrile is greater than for the polymer while many other liquids have  $(\delta_d^2 + \delta_p^2)$  values less than that for PMMA, so acetonitrile forms a cosolvent for PMMA with many liquids.

However, Hansen parameters cannot explain the cosolvent pair formamide and ethanol, both being nonsolvents, and solvent self-association is the reason. Because each liquid is hydrogen bonded ( $\delta_h$  17.6 and 19.4 MPa<sup>1/2</sup> respectively) the extent of bonding to the weakly hydrogen bonding polymer ( $\delta_h \sim 8$  MPa<sup>1/2</sup>) is much less than the maximum possible by that solvent. However, when they are mixed the auto-association is disrupted and the polymer is solvated.

An example of co-nonsolvency is also presented. Poly(methyl methacrylate) dissolves completely in each of butyl chloride and pentyl acetate alone, but not in their mixtures of some intermediate compositions. It appears that charge transfer interaction between chloride and ester groups of the solvents develop at the expense of solvent-polymer interactions.

The next example of the effect of solvent self-association on polymer solubility concerns the swelling of elastomers in various mixtures of methanol and petrol, work carried out in the General Motors laboratories in Warren, Michigan (ref. 12). Except for a fluorocarbon, there is a reasonable correlation between the Hildebrand parameter of each solvent mixture and the extent of polymer swelling. From the Hildebrand parameter values of the methanol-petrol mixtures the fluorocarbon elastomer Viton A should show maximum swell in a mixture containing 15% methanol. Instead, swelling continues to increase, reaching no maximum before 100%

swelling in pure methanol. (This behaviour was not observed in higher alcohols.) The Hansen parameters are more informative (Table 3).

TABLE 3. Hansen parameter values

	$\delta_d/\text{MPa}^{1/2}$	$\delta_p/\text{MPa}^{1/2}$	$\delta_h/\text{MPa}^{1/2}$	$\delta_t/\text{MPa}^{1/2}$
Teflon (similar to Viton)	15.3	7.2	5.3	17.8
Methanol	15.1	12.3	22.3	29.7
Methanol (calculated on basis of full self-association)				20

In mixtures of methanol, petrol and Viton the methanol is self-associated, as there is nothing else with which it can hydrogen bond. The result is that the effective Hildebrand parameter of the mixture is very much lower, resembling an ether rather than an alcohol, and is very similar to that of the fluorocarbon.

Atomic (rather than group) attraction constants are required for the calculation referred to above, but these have not yet been adequately refined, especially for Hansen parameters. In terms of Hildebrand parameters, van Krevelen (ref. 13) developed a set of atomic attraction constants in his work on solvents for coal, and these can be applied to methanol oligomers. The molar attraction,  $F$ , is defined

$$F = \delta V$$

so  $\delta = \frac{\sum z_F/V}{z}$  or  $\frac{\sum z_F/\sum z V}{z}$  for the sum of groups or atoms  $z$ . For methanol ( $V = 40 \text{ cm}^3 \text{ mol}^{-1}$ ) the calculation is shown in Table 5.

TABLE 4. Atomic attraction constants

$z$ (atom)	Bond type	$z_F/\text{cm}^{3/2} \text{ mol}^{-1}$
C		0
H		140
O	ether	256
O	primary alcohol	736

TABLE 5. Calculation of Hildebrand parameter of methanol from atomic attraction constants

$z$ (bond type)	$\sum z_F$
(i) as $\text{CH}_3\text{OH}$	
4H	560
O (alcohol)	736
C	0
	<hr/> 1296 $\text{cm}^{3/2} \text{ mol}^{-1}$
	$\delta = 1296/40 = 32 \text{ MPa}^{1/2}$
(ii) as $\begin{array}{c} \text{O-H} \\   \\ \text{CH}_3 \end{array}$	
4H	560
O (ether)	256
C	0
	<hr/> 816
	$\delta = 816/40 = 20 \text{ MPa}^{1/2}$

It has not yet been emphasized in this review that representing a polymer in Hansen space by a point is a major simplification. A better way of describing the situation is to draw a boundary which is the limit of range of interaction of a polymer with solvents, but one cannot say that the geometric centre of this volume is a unique set of Hansen parameters for the polymer.

This is illustrated by the recent work of Cabasso (ref. 14) on the separation of methanol and hexane by an alloy of compatible polymers, cellulose acetate and polyphosphonate.

It is observed that: polyphosphonate is methanol soluble  
the alloy is methanol insoluble  
hexane is a non-solvent for both

The point in Hansen space representing hexane is some distance from the solubility volumes of the polymers; methanol is within the polyphosphonate area and on the boundary of the cellulose acetate area. It is found that methanol from a methanol/hexane mixture is preferentially sorbed by the alloy in a pervaporation process with a flat sheet membrane. In this case the differences are not minor - hexane and methanol are very different - so the Hansen parameter prediction works even though methanol is self-associated. If methanol were considered as an ether, as in the earlier example, it would still be within the solubility boundary of polyphosphonate, although with much smaller  $\delta_h$  and  $\delta_p$ .

However, in the case of the separation of isomeric xylenes by pervaporation through cellulose ester membranes (ref. 15) Hansen parameters proved inadequate. The selectivity towards different isomers of xylene, with Hansen parameters differing by no more than  $0.4 \text{ MPa}^{1/2}$  (Table 6), cannot be predicted. This is asking too much of cohesion parameters.

TABLE 6. Hansen parameter values of xylene isomers.

	$\delta_d/\text{MPa}^{1/2}$	$\delta_p/\text{MPa}^{1/2}$	$\delta_h/\text{MPa}^{1/2}$	$\delta_t/\text{MPa}^{1/2}$
<i>o</i> -xylene	18.0	1.4	2.9	18.2
<i>m</i> -xylene	17.8	0.8	2.7	18.0
<i>p</i> -xylene	17.8	0.4	2.7	18.0

TABLE 7. Hansen parameter values of cellulose derivatives.

	$\delta_d/\text{MPa}^{1/2}$	$\delta_p/\text{MPa}^{1/2}$	$\delta_h/\text{MPa}^{1/2}$	$\delta_t/\text{MPa}^{1/2}$
cellulose acetate, CA383	16.0	7.2	13.5	22.1
cellulose acetate butyrate, CAB171	16.2	6.6	11.3	20.7
cellulose tripropionate, CTP	17.2	6.3	10.4	21.1

However, Hansen parameters can be used as a guide to selection of membrane materials, with Hansen parameter variations of about  $1 \text{ MPa}^{1/2}$  (Table 7).

The next example concerns the solubility of phenolic antioxidants in polypropylene and polyethylene (ref. 16). From the solubility of the solid phenolic antioxidants in low molecular weight alkanes with known Hildebrand parameter values, Hildebrand parameters for the antioxidants were found to be consistent within  $\pm 0.4 \text{ MPa}^{1/2}$  (Table 8). In contrast, the antioxidant Hildebrand parameters derived from their solubilities in low density polyethylene and polypropylene, and corrected for the free energy required to convert crystalline antioxidant to liquid, deviate by up to  $2 \text{ MPa}^{1/2}$ . The Hildebrand parameters of the antioxidants were also calculated by group contribution methods, and were found to be in the same range as those determined by solubilities in liquids and polymers, but also to show considerable variation.

In this case, where the antioxidant solubility in the polymer is fairly small (of the order of 0.15 to 0.004 % w/w) and they need to be known fairly precisely, Hildebrand parameters are inadequate for reliable prediction, although for some other purposes  $\pm 2 \text{ MPa}^{1/2}$  would be adequate.

TABLE 8. Hildebrand parameters of antioxidants determined by interaction with various solvents.

Solvent, $\delta/\text{MPa}^{1/2}$	Antioxidant $\delta/\text{MPa}^{1/2}$		
	Topanol CA	Ionox 330	Irganox 1010
Octane, 14.4	18.8	17.0	18.6
Dodecane, 15.3	19.2	17.2	19.0
Octadecane, 15.6	19.4	17.4	19.0
Dimethylpentane, 13.7	18.6	16.6	18.0
Pentamethylheptane, 14.8	19.0	16.6	18.4
Polypropylene, 15.2	18.6	15.1	17.0
LD Polyethylene, 15.5	18.2		17.6

As a final example of the limitations of the cohesion parameter approach, consider the results of Takahashi (ref. 17) who has determined Hildebrand parameters of five unsaturated polyester resins (maleic anhydride and succinic acid in varying ratios, two moles of styrene for each mole of maleic anhydride) with different extents of cross-linking (Table 9).

TABLE 9. Hildebrand parameters ( $\text{MPa}^{\frac{1}{2}}$ ) of polyester resins with various degrees of cross-linking.

Method	1	2	3	4	5
	- - - increasing degree of cross-linking - - - →				
Experimental	18.2-20.1	18.1-19.4	18.1-19.4	18.9-22.4	19.1-24.2
Bristow and Watson (ref. 18) (slope and intercept agree)	19.4	19.1	18.8	22.3	24.0
Group contribution					
Small (ref. 19)	20.0	19.8	19.6	19.5	19.3
Hoy (ref. 5)	20.6	20.5	20.3	20.3	20.1
van Krevelen (ref. 13)	17.9	18.2	18.4	18.6	18.6

It is clear that when we are looking for relatively minor differences in behaviour, cohesion parameters might not be appropriate: here even the direction of the change of Hildebrand parameter as a function of cross-linking is uncertain.

The present status of cohesion parameters can be summed up as follows:

- (i) Hildebrand parameters provide a broad, qualitative indication of behaviour for most polymer-solvent systems, with some severe limitations.
- (ii) Hansen parameters and similar sets of partial cohesion parameters give a semi-quantitative measure of the extent of interaction for most polymer-solvent systems, with a few dramatic deviations.
- (iii) A set of interaction cohesion parameters is necessary for a reliable prediction, but values have not yet been determined for most polymers.
- (iv) Extreme caution must be exercised when any of the components is capable of specific interactions, particularly when the components differ greatly in this respect.
- (v) Cohesion parameters cannot be expected to predict relatively minor differences in behaviour.
- (vi) Chromatographic methods hold promise for the evaluation of interaction cohesion parameters.

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