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# The Application of Cohesion Parameters to Wetting and Adhesion—A Review

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Cohesion parameters are quantities with dimensions of (pressure)<sup>1/2</sup> which describe the extent of cohesion within condensed phases. Although the Hildebrand solubility parameter was originally intended to describe the solution properties of liquids which did not undergo any significant mutual chemical interaction, similar cohesion parameters may be applied to the description and prediction of interfacial properties of a wide range of materials. This review outlines the application of cohesion parameters to wetting and adhesion.

## INTRODUCTION

Cohesion parameters provide a measure of the extent of cohesion within condensed materials. Molecular materials exist in the form of liquids or solids over certain ranges of temperature and pressure because in some circumstances these condensed states are more stable than the corresponding gaseous state: there are energetic advantages in the molecules being packed together. In these condensed phases, strong attractive forces exist between the molecules, each molecule being said to have considerable negative potential energy relative to a vapour phase molecule. (Ionic liquids and crystals possess even stronger attractive forces arising from coulombic interactions.) Interfacial and adhesive properties are also closely related to the cohesion parameters of the component materials.<sup>1–43</sup>

In this review, Hildebrand cohesion parameters are defined, and the expansion of the cohesion parameter formalism to dispersion, orientation, induction and Lewis acid-base effects is described. The three-component Hansen parameters (with dispersion, polar, and hydrogen bonding terms) are

shown to provide an approximate description of surface properties. Corresponding surface free energy relationships are then introduced, and the applications of cohesion parameters to a wide variety of adhesion and lubrication situations are summarised.

## COHESION PARAMETERS

If  $U$  is defined as the molar internal energy (the molar potential energy of a material relative to the ideal vapour at the same temperature), then  $U$  has a negative value. It follows, therefore, that the molar cohesive energy (the energy associated with the net attractive interactions of the material and defined as  $-U$ ) has a positive value. The stabilising or cohesive effect in condensed phases can be expressed in terms of the cohesive pressure which is dimensionally identical with the cohesive energy density (cohesive energy per unit volume),

$$c = -U/V \quad (1)$$

Cohesive energy density is the basis of the original definition by Joel H. Hildebrand and Robert L. Scott of what is now generally called the Hildebrand solubility parameter or Hildebrand parameter,

$$\delta = c^{1/2} = (-U/V)^{1/2}. \quad (2)$$

The term "solubility parameter" is too restrictive for a quantity which may be used to correlate a very wide range of physical and chemical properties, including adhesion,<sup>44</sup> and the term "cohesion parameter" has been applied to the group of parameters of dimension (pressure)<sup>1/2</sup> which includes the Hildebrand parameter. The Hildebrand parameter is sometimes denoted the "total" cohesion parameter, because there is a variety of "partial" cohesion parameters associated with various components of the internal energy.

Up to now, cohesion parameters have usually been expressed in units of  $\text{cal}^{1/2} \text{cm}^{-3/2}$ , but from many points of view the most appropriate and convenient unit is  $\text{MPa}^{1/2}$ . This is numerically identical with  $\text{J}^{1/2} \text{cm}^{-3/2}$  or  $\text{MJ}^{1/2} \text{m}^{-3/2}$ , it conforms to the SI conventions, it is of a convenient numerical size ( $1 \text{ cal}^{1/2} \text{cm}^{-3/2} = 2.0455 \text{ MPa}^{1/2}$ ) and it can be written in a compact form.

The Hildebrand cohesion parameters of liquids and polymers may be evaluated by a variety of methods because they are related to so many physical properties. For example, polymer Hildebrand parameter ranges may be determined experimentally by observation of their dissolution behaviour, degree of swelling or other polymer properties in a "spectrum" of solvents with known Hildebrand parameters. Figure 1 shows an example of swelling (in specific volume of solvent imbibed) as a function of solvent  $\delta$  values. In one of

the original applications of cohesion parameters to polymer solutions<sup>46</sup> the Hildebrand parameter was combined with a classification into strong, moderate or poor hydrogen bonding capability, and ranges of values for representative polymers are given in Table 1 in order of increasing  $\delta$ .

## COHESION AND INTERNAL FREE ENERGY

Grunberg and Nissan<sup>48</sup> formulated a relationship between the work of cohesion,  $W$ , and the surface free energy,  $\gamma$ , as follows. If the volume per molecule is  $V/N_A$  ( $V$  = molar volume,  $N_A$  = Avogadro constant), the number of molecules per unit surface area of the liquid is  $(N_A/V)^{2/3}$ . The surface energy per molecule of liquid is  $(N_A/V)^{-2/3}$ , so the molar work of cohesion is

$$W = 2\gamma(N_A/V)^{-2/3}N_A = 2\gamma N_A^{1/3} V^{2/3} \quad (3)$$

The ratio of  $W$  to the cohesion energy,  $-U$ , is a dimensionless constant characteristic of the particular liquid and ranging from about 3.5 for nonpolar liquids to between 4 and 8 for hydrogen-bonded liquids.

In terms of Hildebrand parameter  $\delta$  and cohesive energy density or cohesive

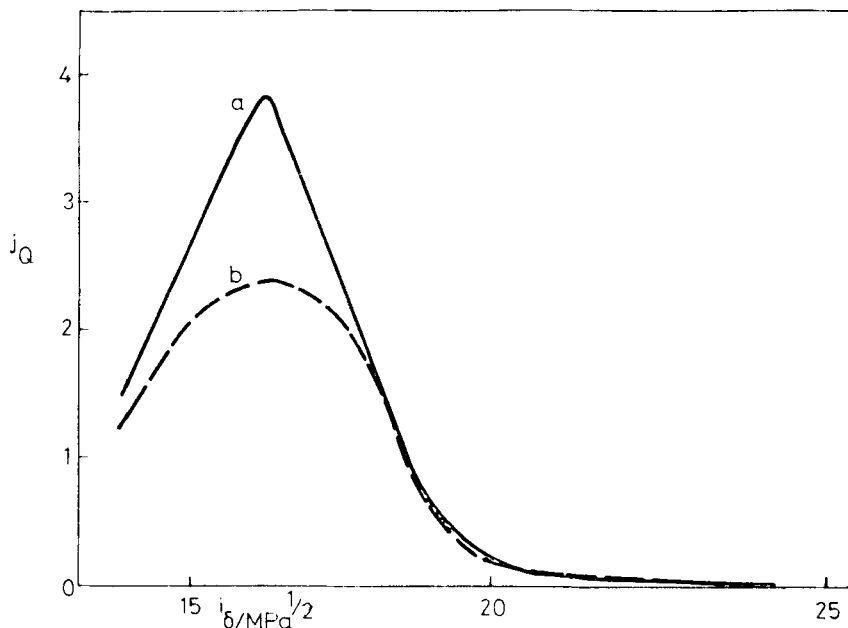


FIGURE 1 Swelling ( $j_Q$ ) of natural rubber as a function of solvent Hildebrand parameter ( $\delta$ ): a, pure gum; b, tyre tread. [Adapted from Mark and Tobolsky.<sup>45</sup>]

TABLE I

Approximate Hildebrand parameter ranges for some common polymeric materials, classified by hydrogen bonding capability and in order of increasing  $\delta$  values. [Adapted from Seymour.<sup>4,7</sup>]

Polymer	Hildebrand parameter ranges $\delta$ /MPa <sup>1/2</sup> in solvents with hydrogen bonding capability which is		
	poor	moderate	strong
Polytetrafluorocarbons	12-13	—	—
Ester gum	14-22	15-22	19-22
Alkyd 45% soy oil	14-22	15-22	19-24
Silicone DC-1107	14-19	19-22	19-24
Poly(vinyl ethyl ether)	14-23	15-22	19-29
Poly(butyl acrylate)	14-26	15-24	—
Poly(butyl methacrylate)	15-23	15-20	19-23
Silicone DC-23	15-17	15-16	19-21
Polyisobutylene	15-16	—	—
Polyethylene	16-17	—	—
Gilsonite®	16-19	16-17	—
Poly(vinyl butyl ether)	16-22	15-21	19-23
Natural rubber	17	—	—
Hypalon 20 [chlorosulfonated PE]	17-20	17-18	—
Ethyl cellulose N-22	16-23	15-22	19-30
Chlorinated rubber	17-22	16-22	—
Dammar gum	17-22	16-21	19-22
Versamid® 100 [polyamide]	17-22	17-18	19-23
Polystyrene	17-22	19	—
Poly(vinyl acetate)	17-19	—	—
Poly(vinyl chloride)	17-23	16-22	—
Phenolic resins	17-24	16-27	19-28
Buna N (butadiene-acrylonitrile copolymer)	18-19	—	—
Poly(methyl methacrylate)	18-26	17-27	—
Carbowax® 4000 [poly(ethylene oxide)]	18-26	17-30	19-30
Thiokol [poly(ethylene sulfide)]	18-21	—	—
Polycarbonate	19-22	19-21	—
Pliolite® P-1230	19-22	—	—
Mylar® [poly(ethylene terephthalate)]	19-22	19-20	—
Vinyl chloride-acetate copolymer	19-23	16-27	—
Polyurethane	20-21	—	—
Styrene-acrylonitrile copolymer	22-23	19-20	—
Vincol® [rosin derivative]	22-24	16-27	19-26
Epon® 1001 [epoxy]	22-24	17-27	—
Shellac	—	21-23	19-29
Polymethacrylonitrile	—	22-23	—
Cellulose acetate	23-26	21-30	—
Nitrocellulose	23-26	16-30	26-30
Polyacrylonitrile	—	25-29	—
Poly(vinyl alcohol)	—	—	25-27
Nylon 66 [poly(hexamethylene adipamide)]	—	—	28-31
Cellulose	—	—	30-33

pressure the relationship is

$$\delta^2 = c = AV^{2/3}\gamma/V = AV^{-1/3}\gamma \quad (4)$$

or

$$A = \delta^2 V^{1/3} \gamma^{-1} \quad (5)$$

where  $A$  is a constant which varies only between certain limits according to the type of molecule<sup>14-16</sup> (Table II). It is noteworthy that such diverse liquids as molten metals and organic liquids have comparable  $A$  values.

This approach is reasonable as long as the area per molecule is proportional to  $V^{2/3}$  (as for spherical molecules), but for polymer molecules it is better to interpret  $\delta$  and  $V$  as the Hildebrand parameter and molar volume of polymer segments or repeat units rather than of whole molecules.

Other empirical equations of a similar nature have been used, for example<sup>27,49</sup>

$$\gamma = k\delta^2 V^{1/3} \quad (6)$$

where  $k = 1.8 \times 10^{-9} \text{ mol}^{1/3}$  according to Siow and Patterson.<sup>40</sup> Schonhorn,<sup>37</sup> Bonn and van Aartsen,<sup>5</sup> Beerbower<sup>3</sup> and Becher<sup>2</sup> used the same equation with different numerical constants. Gordon<sup>50</sup> used the quantity "cohesion" ( $\gamma/V^{1/3}$ ) to estimate the cohesive nature of molten inorganic salts in relation to polar liquids. Hildebrand and Scott<sup>49</sup> proposed the relationship

$$\delta = k(\gamma/V^{1/3})^{0.43} \quad (7)$$

This equation has been widely used. Lee<sup>27</sup> found that 65% of 129 nonpolar and polar liquids obeyed it reasonably well, and it was applied to polymers using for  $V$  the polymer repeat unit volume.<sup>26,51</sup>

An interesting contribution to the development of the link between cohesion

TABLE II

Correlation between Hildebrand parameter ( $\delta$ ), surface free energy ( $\gamma$ ), and molar volume ( $V$ ) of various liquids.  
[Adapted from Gardon and Teas.<sup>14-16</sup>]

Liquid type	$10^{-8}\delta^2 V^{1/3}\gamma^{-1}/\text{mol}^{-1/3}$
Monobasic alcohols, organic acids	8.8-11.6
Water, glycerol, ethylene glycol, cyclohexanol	7.8- 8.2
Other organic liquids	4.9- 6.5
Liquid Na, K, Bi, Pb, Tl, Sn, Ag, Ga, Al, Au, Cu, Fe	5.4- 6.4
Liquid Hg, Cd, Mg, Zn	2.1- 3.5

and adhesion, bulk and surface properties, was made by Prausnitz, Eckert and Sprow.<sup>9,41</sup> The energy of the interphase relative to the ideal gas state was calculated by subtracting the change in energy on forming the surface phase from pure liquid, from the energy of the bulk liquid relative to the ideal gas. Properties of the interfaces could then be determined by assuming that the interphase was a regular solution defining a surface cohesion parameter as the square root of the surface cohesive energy density.

## EXPERIMENTAL SPREADING QUANTITIES

The specific interfacial free energy of a material is the excess free energy per unit area of surface, and in the case of liquid-vapour or solid-vapour interfaces it is known as the specific surface free energy or surface tension, manifested as an internal force which tends to reduce the surface area to a minimum. (The SI unit of surface energy is  $\text{J m}^{-2}$  or  $\text{N m}^{-1}$ , but frequently more convenient is the sub-multiple  $\text{mJ m}^{-2}$  or  $\text{mN m}^{-1}$  which is numerically equivalent to the commonly used c.g.s unit, the  $\text{erg cm}^{-2}$  or  $\text{dyn cm}^{-1}$ .) For a system involving a solid ( $s$ ) and liquid ( $i$ ), Young's equation is (in notation similar to that of Melrose<sup>52</sup>)

$${}^{s,i}\gamma - {}^{i,s}\gamma = {}^i\gamma \cos {}^{is}\theta, \quad (8)$$

where  ${}^{s,i}\gamma$  is the free energy of the interface solid  $s$ -vapour  $i$ ,  ${}^{i,s}\gamma$  is the free energy of the solid  $s$ -liquid  $i$  interface, and  ${}^i\gamma$  is the surface free energy of liquid  $i$  in contact with its vapour. The term  ${}^i\gamma \cos {}^{is}\theta$  is sometimes called the adhesion free energy, wetting free energy, or wetting tension, and this difference between  ${}^{s,i}\gamma$  and  ${}^{i,s}\gamma$  is the quantity which is experimentally determined. The film pressure or equilibrium spreading pressure is

$${}^{s,i}\pi = {}^s\gamma - {}^{s,i}\gamma \quad (9)$$

where  ${}^s\gamma$  is the surface free energy of the solid  $s$  in contact with air or its own vapour, so

$${}^s\gamma = {}^i\gamma \cos {}^{is}\theta + {}^{i,s}\gamma + {}^{s,i}\pi \quad (10)$$

For high energy liquids on smooth, homogeneous, low energy solids such as polymers where  ${}^{is}\theta \gg 0$  it is often assumed that  ${}^{s,i}\pi = 0$ , and

$${}^s\gamma = {}^i\gamma + {}^{i,s}\gamma \quad (11)$$

As  ${}^{is}\theta$  decreases and approaches zero,  ${}^{s,i}\pi$  is often significant and Eq. (11) is then invalid.

Liquids spread when the spreading coefficient ( ${}^s\gamma - {}^i\gamma - {}^{i,s}\gamma$ ) is zero or positive, so wetting is favoured by large  ${}^s\gamma$  (high solid surface free energy), small  ${}^i\gamma$  (low liquid surface free energy), and small  ${}^{i,s}\gamma$  (low  $i-s$  interfacial free energy).

Zisman introduced the concept of the critical surface free energy (or tension) of wetting,  $\gamma_c$ , of a solid.<sup>7,53-56</sup> For a homologous series of some liquids on a given solid the plot of  $\cos \theta$  against  $\gamma$  is a straight line, and  $\gamma_c$  is the value  $\gamma$  at the intercept of the plotted line with the horizontal line defined by  $\cos \theta = 1$ :

$$\cos \theta - \gamma = \gamma_c \quad (12)$$

Thus the critical surface free energy of the solid substrate is the surface free energy of the hypothetical liquid which has  $\cos \theta = 1$  on this solid, and zero solid/liquid surface free energy ( $\gamma = 0$ ). As shown below, in many systems  $\gamma_c$  can be identified with  $\gamma$ . The fundamental importance of  $\gamma_c$  is that liquids having a  $\gamma$  value lower than  $\gamma_c$  will spread on the surface, obeying the general rule that liquids of lower surface free energy spread over materials (liquids or solids) of higher surface free energy, so reducing the total system surface free energy. Not all series of liquids exhibit linear  $\cos \theta - \gamma$  plots<sup>57</sup> but it is possible to use "partial" surface free energy Zisman methods, separating hydrogen bonding and polar interactions from dispersion effects<sup>58,59</sup> to improve the situation.

## GEOMETRIC MEAN APPROXIMATION

Another aspect of the analogy between cohesion energy in bulk materials and free energy of adhesion at interfaces concerns the geometric mean approximation.

In systems where only dispersion or London<sup>60</sup> forces are important, the extent of interaction between molecules depends on the first ionisation potential,  $I$ , and the polarisability,  $\alpha$ , of the  $i$  and  $j$  molecules concerned:

$$-U_d = \frac{3^i I^j I^i \alpha^j \alpha^i}{2(I^i + I^j)r^6} \quad (13)$$

Ionisation potentials,  $I$ , and intermolecular distances,  $r$ , do not usually vary greatly for different pairs of adjacent molecules, and to a good approximation,

$$I^i + I^j \simeq 2(I^i I^j)^{1/2} \quad (14)$$

and

$$r \simeq 2(r^i r^j)^{1/2} \quad (15)$$

This forms the basis of the geometric mean rule for dispersion interactions, which states that the dispersion cohesion energy,  ${}^{ij}U_d$  of a mixture of  $i$  and  $j$  is given by

$${}^{ij}U_d = {}^iU_d^{1/2} {}^jU_d^{1/2} \quad (16)$$



which is a major assumption in cohesion parameter theory. Early in the development of the cohesion parameter concept, the geometric mean assumption was verified by Hildebrand and Carter<sup>61</sup> to within 1% for eight mixtures of carbon tetrahalides. Further tests were made by Scatchard, Wood and Mochel<sup>62</sup> and Staveley, Tupman and Hart,<sup>63</sup> and the geometric mean assumption can be considered to be justified, at least in favourable circumstances, although discussion on its validity continues.<sup>64,65</sup>

Good and Girifalco<sup>17,20,66,67</sup> developed expressions relating the interfacial free energies for two immiscible phases to the surface free energies of the individual phases  $i$  and  $s$ :

$${}^{is}\gamma = {}^i\gamma + {}^s\gamma - 2{}^{is}\Phi({}^i\gamma{}^s\gamma)^{1/2} \quad (17)$$

The value of the interaction parameter  ${}^{is}\Phi$  can be computed from molecular properties, and is close to unity for organic systems such as the wetting of organic polymers by organic liquids. It can be shown that if the equilibrium spreading pressure is zero, Zisman's critical surface energy  $\gamma_c$  is related to  ${}^s\gamma$  by

$${}^s\gamma = \gamma_c/{}^{is}\Phi^2 \quad (18)$$

so that  ${}^s\gamma$  and  $\gamma_c$  are equal when  ${}^{is}\Phi = 1$ . The close relationship between  ${}^s\gamma$  and  $\gamma_c$  implied by this equation explains the success in the correlation of  $\gamma_c$  and the Hildebrand parameter<sup>7,13,14,25,26,28,55</sup> although in some situations it is claimed that  $\gamma_c$  is more useful in correlations than  $\delta$ .<sup>68</sup>

The disadvantage of the geometric mean equation and relationships derived from it is that calculations of  ${}^{is}\Phi$  values are complex. A harmonic mean equation (for low surface energy systems) or a geometric-harmonic mean equation (for high surface energy systems) is sometimes preferred.<sup>69</sup> These involve the division of surface free energy into dispersion and polar components, as described below.

## EXPANDED COHESION PARAMETER FORMALISM

The Hildebrand parameter is appropriate only for the description of the properties of materials not exhibiting polar interactions and specific chemical interactions such as hydrogen bonding. To be generally useful, theories or models attempting to systematise the behaviour of matter must deal with molecular interactions by providing information about their natures or origins as well as about their strengths. The cohesive properties characteristic of the condensed states of matter are produced by a variety of intermolecular forces.

Dispersion or London<sup>60</sup> forces, arising from the fluctuating dipoles which result from a positive nucleus and a negative electron cloud in each atom,

occur in all molecules, whether polar or not. Their origin is the instantaneous electrical dissymmetry of electrons in one molecule polarising the electron clouds in adjacent molecules, and inducing instantaneous dipoles of opposite polarity, resulting in intermolecular attraction. Although the molecules continue to rotate and so change the dipole direction, one molecule tends to follow the other, and because of this correlation the attractive effect does not average to zero. The dispersion cohesive pressure of a pure material  $i$  is denoted  ${}^i c_d$ , and the corresponding cohesion parameter,  ${}^i \delta_d$  is defined by

$${}^i U_d / {}^i V = {}^i c_d = {}^i \delta_d^2 \quad (19)$$

It can be shown on the basis of London theory that the nonpolar, dispersive interactions between unlike molecules of type  $i$  and type  $j$  provide a contribution to the cohesive pressure which is based on the geometric mean of the individual values and is given by

$${}^{ij} c_d = ({}^i c_d {}^j c_d)^{1/2} = {}^i \delta_d {}^j \delta_d \quad (20)$$

A simple interpretation of this "geometric mean" behaviour is that the interaction is of a "symmetrical" nature: each member of a pair of molecules interacts by virtue of the same property, the polarisability. For nonpolar molecules, dispersion forces make the only contributions to cohesive pressure.

Orientation effects result from dipole-dipole or Keesom<sup>70</sup> interactions, and occur between molecules which have permanent dipole moments, one dipole tending to align the other into an energetically favourable arrangement. The orientation cohesive pressure of a pure material  $i$  is denoted  ${}^i c_o$ , and the corresponding orientation cohesion parameter,  ${}^i \delta_o$ , is defined by

$${}^i U_o / {}^i V = {}^i c_o = {}^i \delta_o^2 \quad (21)$$

Like dispersion forces, these are "symmetrical" interactions, depending on the same property of each molecule, which in this case is the dipole moment. It follows that the geometric mean rule is obeyed well for orientation interactions between unlike molecules<sup>71</sup> and for polar molecules which may be represented by spherical force fields with small ideal dipoles at their centres, this contribution to the cohesive pressure in mixtures of  $i$  and  $j$  molecules is

$${}^{ij} c_o = ({}^i c_o {}^j c_o)^{1/2} = {}^i \delta_o {}^j \delta_o \quad (22)$$

Dipole induction effects arise from dipole-induced dipole or Debye<sup>72</sup> interactions, occurring between molecules with permanent dipole moments and any other neighbouring molecules, whether polar or not, and resulting in an induced non-uniform charge distribution. The induced and permanent dipoles are mutually attracted, and the thermal molecular motion does not disorientate the direction of the induced moment from that of the inducing moment because the electric moment adjusts simultaneously and is in-

dependent of molecular rotation. (The extent of the interaction, of course, depends on the concentration of polarisable molecules, and this is expressed in terms of the relative permittivity). In contrast to dispersion and orientation interactions, dipole induction interactions are “unsymmetrical”, involving the dipole moment of one molecule and the polarisability of the other. Consequently, the cohesive pressure term for induction in a pure material  $i$  involves the product  ${}^i\delta_i{}^i\delta_a$ , where  ${}^i\delta_i$  is the induction cohesion parameter. Similarly, in a mixture of  $i$  and  $j$ ,

$${}^{ij}c = {}^i\delta_i{}^j\delta_d + {}^j\delta_j{}^i\delta_d \quad (23)$$

Lewis acid-base or electron donor-acceptor interactions have been reviewed frequently.<sup>73-78</sup> The Lewis acid-base complex is formed by an overlap between a filled orbital of sufficiently high energy in the donor molecule and a vacant orbital of sufficiently low energy (high electron affinity) in the acceptor molecule. This type of interaction differs from a “normal” chemical bond in that only one molecule (the donor) supplies the pair of electrons, rather than each molecule supplying one electron. More than one electron must be involved and co-ordination of the Lewis acid to the Lewis base must occur. Many authors have pointed out that acid-base cohesion parameters can be expressed in terms of electron donating and accepting properties.<sup>79-83</sup> Lewis acid-base interactions are “unsymmetrical”, involving a donor and an acceptor with different roles (rather than two equivalent participants, as is the case in dispersion interactions). It is apparent, therefore, that it is necessary to use two separate parameters to characterise these interactions, and this may be done in terms of a Lewis acid cohesion parameter,  $\delta_a$ , and a Lewis base cohesion parameter,  $\delta_b$ , in a manner analogous to that for induction interactions. The maximum acid-base interaction occurs when  ${}^i\delta_a = {}^j\delta_b = 0$  or when  ${}^j\delta_a = {}^i\delta_b = 0$ . In these situations the products  ${}^j\delta_a{}^i\delta_b$  or  ${}^i\delta_a{}^j\delta_b$  correspond to exothermic interactions, in contrast to athermic or endothermic processes which are the only possibilities when interactions are restricted to dispersion and polar forces.

Hydrogen bonding interactions are another kind of donor-acceptor interaction or association, a special type of Lewis acid-base reaction with the electron acceptor being called a Brönsted acid. One definition is that a hydrogen bond is a second bond formed to another atom by a covalently bound hydrogen atom. It is apparent that it is necessary to use two separate parameters to characterise these interactions, and this may be done using the Lewis acid-base cohesion parameters  $\delta_a$  and  $\delta_b$ .

One of the assumptions central to the cohesion parameter approach is that the various contributions to cohesive pressure are additive. For a pure material  $i$ , the Hildebrand or total cohesion parameter is related to the

interaction parameters by

$${}^i\delta_t^2 = {}^i\delta_d^2 + {}^i\delta_o^2 + 2{}^i\delta_i^i\delta_d + 2{}^i\delta_a^i\delta_b. \quad (24)$$

Numerical values of these interaction cohesion parameters for a few common liquids are presented in Table III.

### THREE COMPONENT HANSEN PARAMETERS

C. M. Hansen<sup>85-87</sup> proposed an extension of the Hildebrand parameter method to polar and hydrogen bonding systems which is simpler to use.

It is assumed that dispersion, polar, and hydrogen bonding parameters are valid simultaneously, related by the equation

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2, \quad (25)$$

with values of each component parameter being determined empirically on the basis of many experimental observations (Table IV). Hansen's total cohesion parameter,  $\delta_t$ , corresponds to the Hildebrand parameter, although the two quantities should not be expected to be identical because they are determined by different methods.

Theoretical justification for application of cohesion parameters of this type is not strong, and is further weakened by the doubling of the scale on the dispersion axis with the aim of providing approximately spherical "volumes" of interaction when plotted on  $(\delta_d, \delta_p, \delta_h)$  co-ordinates (Figure 2). In the case of solubility, the distance of the solvent co-ordinates  $({}^i\delta_d, {}^i\delta_p, {}^i\delta_h)$  from the centre point  $({}^j\delta_d, {}^j\delta_p, {}^j\delta_h)$  of the solute sphere of solubility is

$${}^{ij}R = [4({}^i\delta_d - {}^j\delta_d)^2 + ({}^i\delta_p - {}^j\delta_p)^2 + ({}^i\delta_h - {}^j\delta_h)^2]^{1/2} \quad (26)$$

This distance can be compared with the radius  ${}^jR$  of the solute sphere of solubility, and if

$${}^{ij}R < {}^jR,$$

the likelihood of the solvent  $i$  dissolving the solute  $j$  is high. This works well, despite the fact that there is limited theoretical justification. The "sphere" can be projected on to the three planes passing through two axes and the origin, to provide circles in two-dimensional graphs, as illustrated in Figure 2. The incorporation of the numerical factor 4 does not appear to be necessary to provide a spherical interaction volume;<sup>91,92</sup> the apparent non-spherical representation is the result of the restricted range of  $\delta_d$  values compared with the  $\delta_p$  and  $\delta_h$  ranges.

In some applications, only two of the three Hansen parameters are used, so that the locations of materials may be displayed on two-dimensional projected

TABLE III

Interaction cohesion parameters of liquids in order of increasing Hildebrand parameter.  
 [Adapted from Karger, Snyder, Eon and Horvath.<sup>84</sup>]

Liquid	$\delta/\text{MPa}^{1/2}$						$V/\text{cm}^3 \text{ mol}^{-1}$
	$\delta_t$	$\delta_d$	$\delta_o$	$\delta_i$	$\delta_a$	$\delta_b$	
Perfluoroalkanes	ca.12	ca.12	—	—	2.1	—	—
<i>n</i> -Pentane	14.5	14.5	—	—	—	—	115
Di-iso-propyl ether	14.5	14.1	2.1	0.2	—	6.1	102
<i>n</i> -Hexane	14.9	14.9	—	—	—	—	131
Diethyl ether	15.3	13.7	4.9	1.0	—	6.1	105
Triethylamine	15.3	15.3	—	—	—	9.2	140
Cyclohexane	16.8	16.8	—	—	—	—	108
Propyl chloride	17.2	14.9	5.9	1.2	—	1.4	88
Carbon tetrachloride	17.6	17.6	—	—	—	1.0	97
Diethyl sulfide	17.6	16.8	3.5	0.5	—	5.3	108
Ethyl acetate	18.2	14.3	8.2	2.1	—	5.5	98
Propylamine	18.2	14.9	3.5	0.4	3.7	11.3	82
Ethyl bromide	18.2	16.0	6.3	1.2	—	1.6	77
Toluene	18.2	18.2	—	—	—	1.2	107
Tetrahydrofuran	18.6	15.5	7.2	1.6	—	7.6	82
Benzene	18.8	18.8	—	—	—	1.2	89
Chloroform	19.0	16.6	6.1	1.0	13.3	1.0	81
Ethyl methyl ketone	19.4	14.5	9.6	2.5	—	6.5	90
Acetone	19.6	13.9	10.4	3.1	—	6.1	74
1,2-Dichloroethane	19.8	16.8	8.6	1.0	—	1.4	79
Anisole	19.8	18.6	4.3	0.8	—	3.5	109
Chlorobenzene	19.8	18.8	3.9	0.6	—	2.1	102
Bromobenzene	20.2	19.6	3.1	0.4	—	2.1	105
Methyl iodide	20.2	19.0	5.1	0.6	—	1.4	62
Dioxane	20.7	16.0	10.6	2.1	—	9.4	86
Hexamethylphosphoramide	21.5	17.2	7.0	3.5	—	8.2	176
Pyridine	21.7	18.4	7.8	2.1	—	10.0	81
Acetophenone	21.7	19.6	5.5	1.4	—	6.8	117
Benzonitrile	21.9	18.8	7.0	2.1	—	4.7	103
Propionitrile	22.1	14.1	13.5	3.7	—	4.3	71
Quinoline	22.1	21.1	3.7	0.6	—	8.6	118
<i>N,N</i> -Dimethylacetamide	22.1	16.8	9.6	3.3	—	9.2	92
Nitroethane	22.5	14.9	12.3	4.5	—	2.1	71
Nitrobenzene	22.7	19.4	7.4	2.3	—	2.1	103
Tricresylphosphate	23.1	19.6	5.1	3.1	—	(?)	316
Dimethylformamide	24.1	16.2	12.7	4.9	—	9.4	77
Propanol	24.5	14.7	5.3	0.8	12.9	12.9	75
Dimethylsulfoxide	24.5	17.2	12.5	4.3	—	10.6	71
Acetonitrile	24.7	13.3	16.8	5.7	—	7.8	53
Phenol	24.7	19.4	4.7	0.8	19.0	4.7	92
Ethanol	26.0	13.9	7.0	1.0	14.1	14.1	59
Nitromethane	26.4	14.9	17.0	6.1	—	2.5	54
$\gamma$ -Butyrolactone	26.4	16.4	14.7	6.5	—	(?)	77
Propylene carbonate	17.2	20.0	12.1	4.9	—	(?)	85
Diethylene glycol	29.2	16.8	8.2	1.2	10.8	10.8	96
Methanol	29.7	12.7	10.0	1.6	17.0	17.0	41
Ethylene glycol	34.8	16.4	13.9	2.3	12.5	12.5	56
Formamide	39.3	17.0	(?)	(?)	(large)	(large)	40
Water	47.9	12.9	(?)	(?)	(large)	(large)	18

TABLE IV

Hansen parameters for liquids and polymers at 25°C, based on Hansen's 1971 data.  
 [Selected from Hansen and Beerbower,<sup>88</sup> Hansen,<sup>87</sup> Ramsbotham<sup>89</sup> and Shell.<sup>90</sup>]

	$V/\text{cm}^3 \text{mol}^{-1}$	$\delta/\text{MPa}^{1/2}$		
		$\delta_d$	$\delta_p$	$\delta_h$
<i>n</i> -Butane	101.4	14.1	0.0	0.0
<i>n</i> -Decane	195.9	15.8	0.0	0.0
Benzene	89.4	18.4	0.0	2.0
Styrene	115.6	18.6	1.0	4.1
Bromoethane	76.9	15.8	3.1	5.7
Tetrachloromethane	97.1	17.8	0.0	0.6
Diethyl ether	104.8	14.5	2.9	5.1
Acetone	74.0	15.5	10.4	7.0
Benzaldehyde	101.5	19.4	7.4	5.3
Ethyl acetate	98.5	15.8	5.3	7.2
Acetonitrile	52.6	15.3	18.0	6.1
Pyridine	80.9	19.0	8.8	5.9
Methanol	40.7	15.1	12.3	22.3
Ethanol	58.5	15.8	8.8	19.4
Acetic acid	57.1	14.5	8.0	13.5
Water	18.0	15.6	16.0	42.3
Cellulose acetate		18.6	12.7	11.0
Nitrocellulose		15.4	14.7	8.8
Polystyrene		21.3	5.8	4.3
Poly(vinyl acetate)		20.9	11.3	9.6

maps. Figure 3 shows the range of  $\delta_p$ - $\delta_h$  locations for major solvent groups, regions of overlap indicating mutual miscibility.

## PARTIAL SURFACE FREE ENERGY PARAMETERS

Equation (6) for surface free energy in terms of Hildebrand parameter,

$$\gamma = k\delta^2 V^{1/3}$$

is expected to be valid only for nonpolar, nonassociated liquids, and partial cohesion parameters are more likely to be generally useful. Beerbower<sup>3</sup> used Hansen parameters, and found different relationships for various classes of liquids:

$$\text{for non-alcohols, } \delta_d^2 + 0.63 \delta_p^2 + 0.63 \delta_h^2 = 59V^{-1/3}\gamma \quad (27)$$

$$\text{for most alcohols, } \delta_d^2 + \delta_p^2 + 0.06 \delta_h^2 = 59V^{-1/3}\gamma \quad (28)$$

$$\text{for acids, phenols, amines, } \delta_d^2 + 2\delta_p^2 + 0.48 \delta_h^2 = 59V^{-1/3}\gamma \quad (29)$$

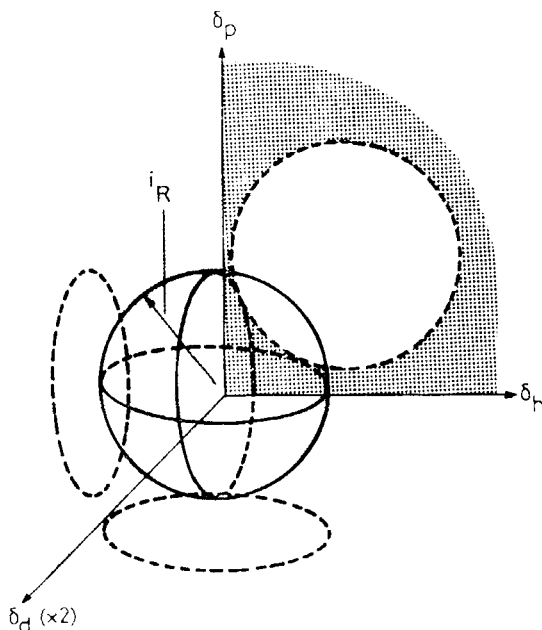


FIGURE 2 Representation of a Hansen parameter solubility sphere with radius of interaction  $R$  and projections on three axial planes. [Adapted from Hansen and Beerbower.<sup>88</sup>]

Koenhen and Smolders,<sup>23</sup> for a wide range of liquids including monofunctional hydrogen bonding systems but excluding some cyclic compounds, acetonitrile, carboxylic acids and polyfunctional alcohols, found

$$\delta_d^2 + \delta_p^2 = 58V^{-1/3}\gamma \quad (30)$$

They attributed the absence of a dependence on  $\delta_h$  in this relationship to the liquid-vapour interfacial interaction not involving hydrogen bonding.

Considerations such as these lead to the suggestion that it may be possible to divide surface free energies up in the same way as cohesion parameters. One set of "partial surface free energies" could be defined by

$$\delta_d = k_d V^{-1/3}\gamma_d, \quad \delta_p = k_p V^{-1/3}\gamma_p, \quad \delta_h = \gamma_h = 0 \quad (31)$$

There is considerable theoretical and experimental justification for subdividing the surface free energy into additive components analogous to the partial cohesion parameter components described above, and for relating the two sets of properties.<sup>1,3,7,10,15,23,27,29,58,59,66,69,88,94-106</sup>

Various models have been used, including

- i) that of Koenhen and Smolders<sup>23</sup> which has already been described:

$$\gamma = \gamma_d + \gamma_p \quad (32)$$

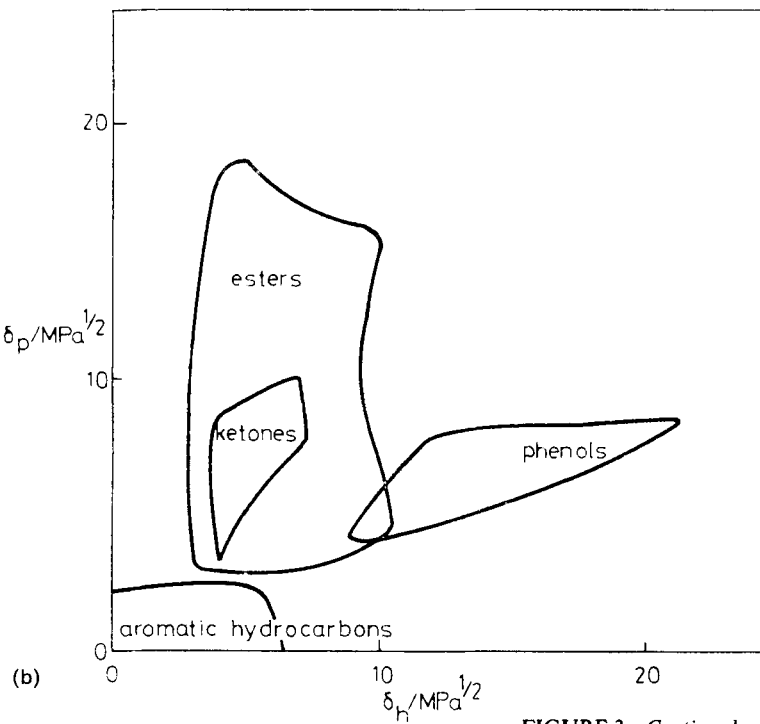
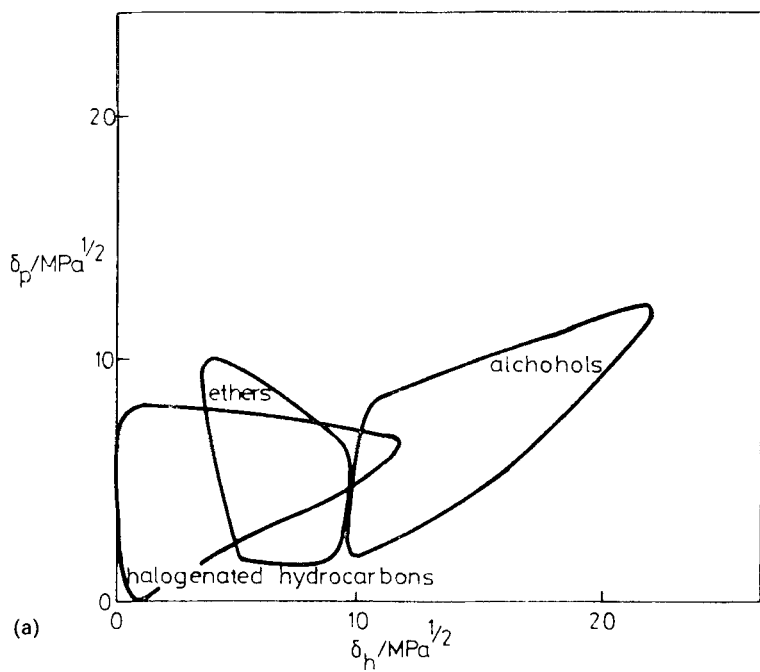
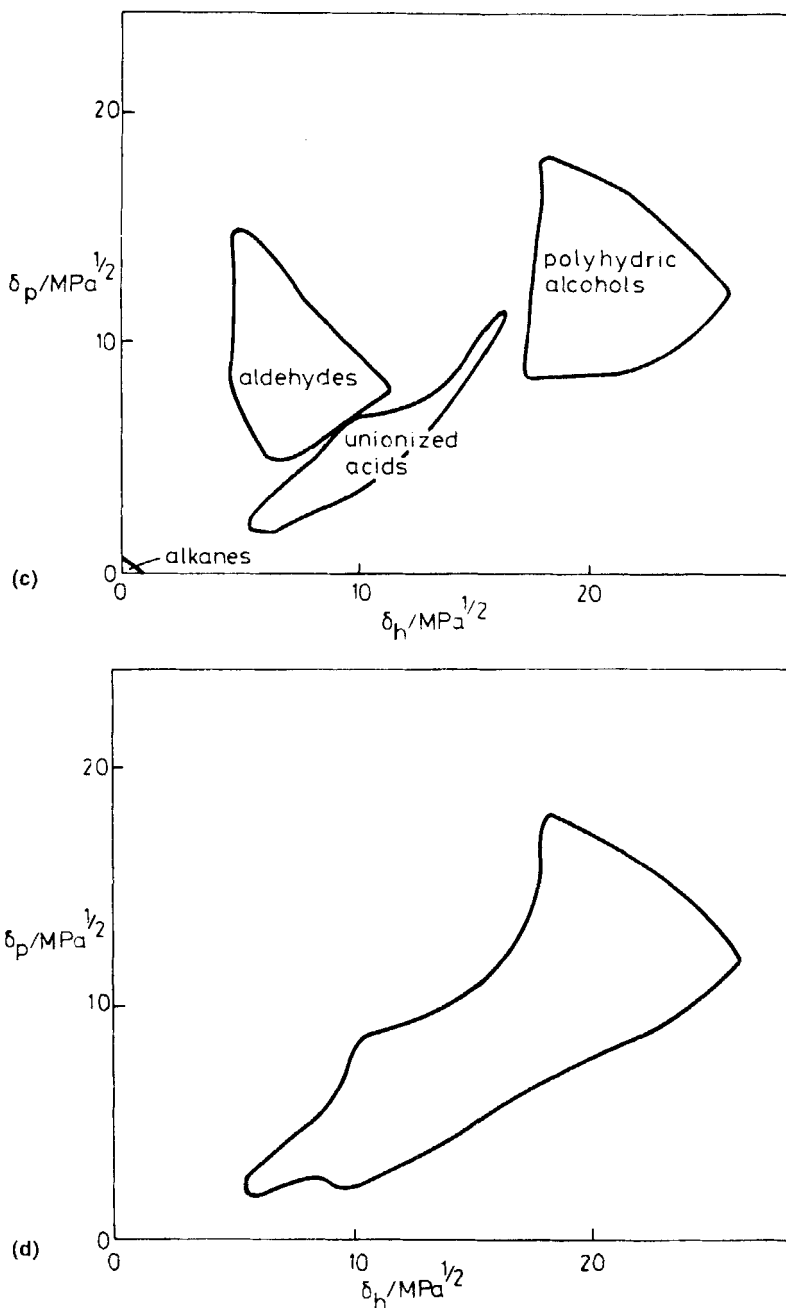


FIGURE 3 Continued overleaf





**FIGURE 3** Hansen parameter  $\delta_p - \delta_h$  locations for major solvent groups : a, ethers, halogenated hydrocarbons and alcohols ; b, esters, aromatic hydrocarbons, ketones and phenols ; c, aldehydes, polyhydric alcohols, unionised acids and alkanes ; and d, proton donor species (acids, phenols, amines, alcohols, polyhydric alcohols). [Adapted from Klein, Eichelberger, Eyer and Smith.<sup>93</sup>]

ii) addition of hydrogen bonding term :

$$\gamma = \gamma_d + \gamma_p + \gamma_h \quad (33)$$

iii) separation of dispersion, dipole-dipole (orientation), induction and hydrogen bonding :

$$\gamma = \gamma_d + \gamma_o + \gamma_i + \gamma_h \quad (34)$$

iv) incorporation of separate Lewis acid and Lewis base terms.<sup>97,98</sup>

Because of the empirical and rather arbitrary way in which the partial cohesion parameters are evaluated, precise correlation with the partial surface free energy terms is not to be expected, but agreement is reasonably good.<sup>59,69</sup>

Hansen<sup>56,99,107,108</sup> considered the characterisation of surfaces in terms of the liquids which spread spontaneously on them, in contrast to those liquids which yield contact angles, and described by Hansen parameters. The results were expressed in the same way as those of solubility studies, with values of  ${}^s\delta_d$ ,  ${}^s\delta_p$ ,  ${}^s\delta_h$  and  ${}^sR$  reported for each surface. These can be used in conjunction with liquid data to evaluate  ${}^{sl}R$ :

$${}^{sl}R^2 = 4({}^s\delta_d - {}^l\delta_d)^2 + ({}^s\delta_p - {}^l\delta_p)^2 + ({}^s\delta_h - {}^l\delta_h)^2 \quad (35)$$

Liquids for which  ${}^{sl}R \leq {}^sR$  are expected to wet the surface, and liquids with coordinates on the spherical boundary surface,  ${}^{sl}R = {}^sR$ , correspond to critical surface free energies. The results for some surfaces appear in Table V. As in the "solubility sphere" studies, the spherical boundaries correspond to situations where there is a predicted zero free energy change for the wetting process. Although cohesion parameters ignore entropy factors and do not provide this kind of information directly, the limiting boundary conditions correspond to  $\Delta H = T\Delta S$  for the adsorption process.

It is also possible to use only the polar and hydrogen bonding Hansen components by drawing a circle with wetting radius  ${}^sR$  on a plot of  $\delta_p$  against  $\delta_h$  points for various liquids, or of  $\delta_p - \delta_h$  lines for liquid mixtures, as illustrated in Figure 4. This example uses the liquid series: ethyl benzene, tetralin, chlorobenzene, *o*-dichlorobenzene, cyclohexanone, acetone, *N*-methyl-2-pyrrolidone, dimethylformamide, dimethyl sulfoxide, 2-pyrrolidone, ethylene cyanohydrin, formamide and water (line A) and ethanol-water mixtures (line B). The critical surface free energy as measured by the series of individual liquids is  $44 \text{ mJ m}^{-2}$ , and  $32 \text{ mJ m}^{-2}$  from ethanol-water mixtures. For Epanol<sup>®</sup> resin 55-B-40 (Figure 5) most of the liquids attacked the substrate, as shown by the fact that the solubility circle overlaps the wetting circle, and these data (A) are not useful. The ethanol-water mixture (B) did yield a critical surface free energy value ( $27 \text{ mJ m}^{-2}$ ), as this region is outside the solubility circle.

TABLE V

Values of Hansen parameters and critical wetting sphere radius for surfaces.  
 [Sources: Hansen and Pierce<sup>99,108</sup> and Panzer.<sup>59</sup>]

Surface	${}^s\delta_d/\text{MPa}^{1/2}$	${}^s\delta_p/\text{MPa}^{1/2}$	${}^s\delta_h/\text{MPa}^{1/2}$	${}^sR/\text{MPa}^{1/2}$
Polyester/melamine	10.2	1.2	10.6	17.8
Polyester/melamine/ polyvinylidene fluoride	16.6	1.8	3.5	5.5
Polyvinylidene fluoride	13.7	10.6	8.2	14.7
Polypropylene (high M.W.)	16.6	-2.3	1.0	11.7
"Tin plate" (chrome-chrome oxide), Sample A	10.2	-0.6	10.6	19.8
Sample B	14.1	-0.4	12.9	16.8
Bonderite® 1000 (iron phosphate, Parker Division, Hooker Chem)	14.7	3.3	5.5	19.0
Epanol® resin 55-B-40 (Shell Chemicals)	18.0	0.4	9.2	18.8
Poly(methylmethacrylate) (Cast Optics, Hackensack)	16.4	6.6	9.2	
Versamid® 930 polyamide (General Mills)	16.8	5.1	8.0	
Lithium stearate	15.65	7.2	17.7	(bimodal)
	15.71	9.4	3.9	
N-octacosane	16.2	1.8	3.3	

A related method of surface characterisation is used in the Meseran surface analyzer technique<sup>109</sup> which is based on the degree of retention on the surface of carbon-14 tagged molecules of three bonding types: tridecane, tetrabromoethane, and diethylsuccinate. A two-dimensional chart is used, with one axis providing Meseran data obtained by subtracting tridecane from diethylsuccinate radioactivity counts and the other recording tetrabromoethane minus tridecane data. The result is that points corresponding to surfaces of particular organic contaminants on metal surfaces, for example, are distributed on the chart according to their polarity characteristics. This empirical method does not actually use cohesion parameters, but the principle is very similar.

Other variations of partial surface free energy-partial cohesion parameter properties have been used, for example:

correlation of  $\gamma_c$  with  ${}^s\delta_d$  for polymers<sup>38,106</sup>

use of  ${}^s\gamma_d$  and  $\delta_d$  for nonpolar polymers<sup>23</sup>

description of surface free energy properties of polysiloxanes<sup>28</sup> and fluorocarbons in terms of polar and nonpolar components

Just as the geometric mean equation (16) for cohesion pressure holds only

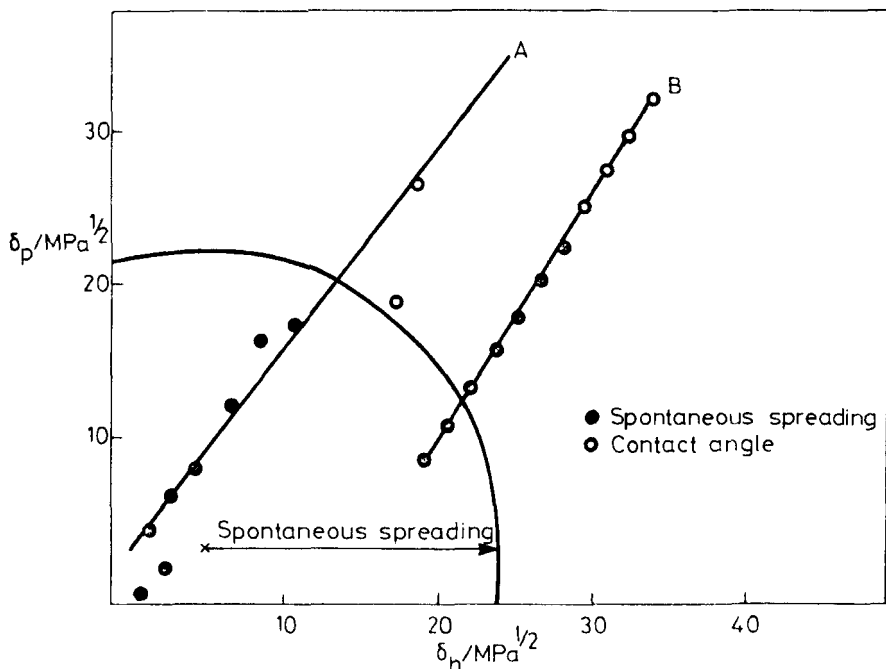


FIGURE 4 Surface evaluation of Bonderite® 1000 (iron phosphate, Parker Division, Hooker Chemical Corporation) (with wetting sphere parameters  $\delta_d = 14.7 \text{ MPa}^{1/2}$ ,  $\delta_p = 3.3 \text{ MPa}^{1/2}$ ,  $\delta_h = 5.5 \text{ MPa}^{1/2}$ ,  $^sR = 19.0 \text{ MPa}^{1/2}$ ) using a series of polar liquids (A) and ethanol-water mixtures (B). Filled circles indicate that spontaneous spreading occurred. [Adapted from Hansen and Pierce.<sup>108</sup>]

for nonpolar, noninteracting systems, Eq. (17) is theoretically justified only for the dispersion component of surface free energy. This problem has been approached in various ways. The dimensionless parameter  $^{is}\Phi$  can be expressed in terms of fractional contributions to the cohesive energies of the components<sup>66</sup>:

$$^{is}\Phi = \left( \frac{{}^sC_d {}^iC_d}{{}^sC {}^iC} \right)^{1/2} + \left( \frac{{}^sC_o {}^iC_o}{{}^sC {}^iC} \right)^{1/2} + \left( \frac{{}^sC_i {}^iC_i}{{}^sC {}^iC} \right)^{1/2} \quad (36)$$

where  $C = C_d + C_o + C_i$ , denoting cohesive energy terms which are closely related to the familiar cohesive pressure  $c$ . It can be seen from equation (36) that if there is a good match between the  $C$  values of the components, the interaction parameter  $^{is}\Phi$  is close to unity, but it is less than unity if the contributions to dispersion, induction and orientation of the surface  $s$  and the liquid  $i$  are mismatched.

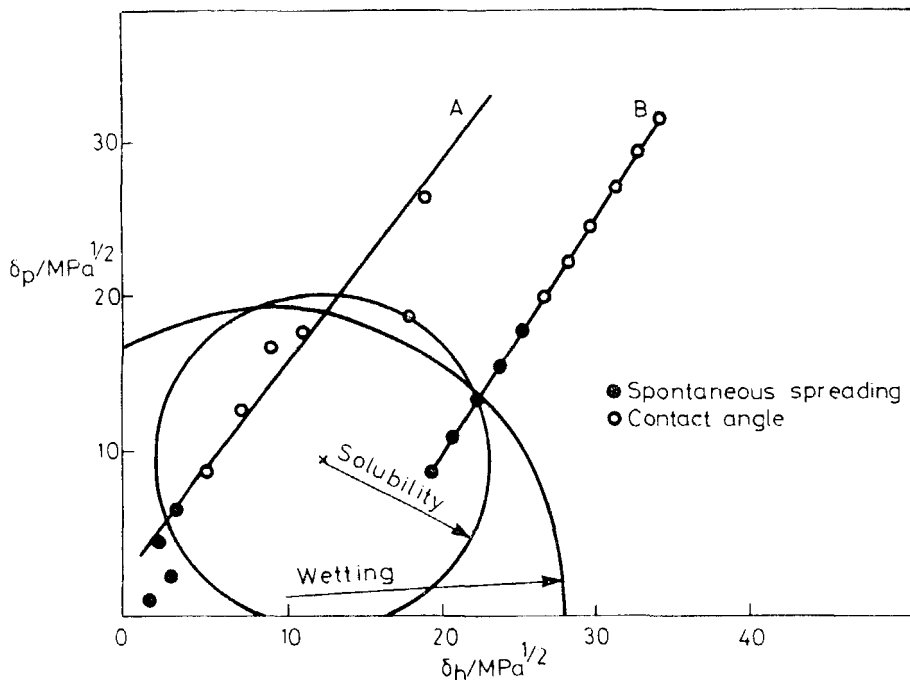


FIGURE 5 Surface evaluation of Epanol<sup>(H)</sup> resin 55-B-40 (Shell Chemical Co.) with wetting parameter  $\delta_d = 18.0 \text{ MPa}^{1/2}$ ,  $\delta_p = 0.4 \text{ MPa}^{1/2}$ ,  $\delta_h = 9.2 \text{ MPa}^{1/2}$ ,  $^sR = 18.8 \text{ MPa}^{1/2}$ ) using a series of polar liquids (A) and ethanol-water mixtures (B). The  $\delta_p - \delta_h$  solubility curve for the resin is also shown ( $\delta_d = 20.7 \text{ MPa}^{1/2}$ ,  $\delta_p = 9.4 \text{ MPa}^{1/2}$ ,  $^sR = 10.8 \text{ MPa}^{1/2}$ ). Filled circles indicate that spontaneous spreading occurred. [Adapted from Hansen and Pierce.<sup>108</sup>]

Another possible modification to Eq. (16) is

$${}^i s_\gamma = {}^i \gamma + {}^s \gamma - 2({}^i \gamma_d {}^s \gamma_d)^{1/2} - {}^i s E \quad (37)$$

where  ${}^i s E$  is a "correction" term which has been given various forms by different authors such as Fowkes,<sup>97</sup> Kloubek<sup>103</sup> and Owens and Wendt.<sup>58</sup> For example,

$${}^i s_\gamma = {}^i \gamma + {}^s \gamma - 2({}^i \gamma_d {}^s \gamma_d)^{1/2} - 2({}^i \gamma_p {}^s \gamma_p)^{1/2} \quad (38)$$

An alternative to the geometric mean equation is the harmonic mean expression,

$${}^i s_\gamma = {}^i \gamma + {}^s \gamma - \frac{4{}^i \gamma_d {}^s \gamma_d}{{}^i \gamma_d + {}^s \gamma_d} - \frac{4{}^i \gamma_p {}^s \gamma_p}{{}^i \gamma_p + {}^s \gamma_p} \quad (39)$$

which has been applied to water, organic liquids, solid and molten polymers and organic pigments.<sup>69</sup> The geometric-harmonic mean equation is

$${}^{is}\gamma = {}^i\gamma + {}^s\gamma - 2({}^i\gamma {}^s\gamma)^{1/2} - \frac{4{}^i\gamma {}^s\gamma {}^p\gamma}{{}^i\gamma {}^p\gamma + {}^s\gamma {}^p\gamma} \quad (40)$$

Similar equations with  $\gamma_n$  replacing  $\gamma_p$  have also been used<sup>58,105</sup> and quantities defined as the square root of  $\gamma_d$ ,  $\gamma_p$ , etc, directly analogous to  $\delta_d$ ,  $\delta_p$ , etc, may be employed.<sup>102,110</sup>

In the case of two liquids  $i$  and  $j$  the liquid-liquid interfacial free energy  ${}^{ij}\gamma$  in principle can be deduced from the individual surface free energy  ${}^{ij}\gamma$  in principle can be deduced from the individual surface free energies  ${}^i\gamma$  and  ${}^j\gamma$  by an equation analogous to Eq. (17):

$${}^{ij}\gamma = {}^i\gamma + {}^j\gamma - 2{}^{ij}\Phi({}^i\gamma {}^j\gamma)^{1/2} \quad (41)$$

${}^{ij}\Phi$  can be evaluated from molecular properties with the aid of relationships deduced theoretically, for example those presented by Girifalco and Good<sup>17</sup> who have tabulated  ${}^{ij}\Phi$  values for water-organic liquids (Table VI) and for mercury-nonmetallic liquids (Table VII). Alternatively, partial surface free energies may be used.<sup>11,97</sup>

The same type of procedure has been extended to polymer-polymer interfaces<sup>111,112</sup> making use of the Flory interaction parameter and the Flory-Huggins lattice model which takes into account deviations in polymer solution properties due to size differences. Discussion of polymer-polymer interfacial properties in terms of partial surface free energies is of particular importance in adhesive bonding and fracture.<sup>102,110,113</sup>

## WETTING AND ADHESION

An important group of practical surface properties involve "wetting" (spontaneous spreading of an applied liquid droplet on a surface) and "dewetting" (the breaking up or "crawling" of an applied film). In the former case the concern is with advancing contact angles, and in the latter with receding contact angles, and the absence of contact angle ( $\theta = 0^\circ$ ) is desirable in practical coatings applications in both cases. The Zisman critical surface free energy has been particularly useful, but cohesion parameter methods have also been applied to various situations, including the wetting properties of:

- coatings<sup>28,86,99</sup>
- elastomers and copolymers<sup>51</sup>
- powder surfaces<sup>31</sup>
- lubricants<sup>3,114,115</sup>
- molten polymers<sup>69</sup>

TABLE VI  
Interaction parameter  ${}^i\Phi$  for water-organic liquid interfaces at 20°C.  
[Source: Girfalco and Good<sup>17</sup>]

Liquid	${}^i\Phi$	Liquid	${}^i\Phi$
<i>Alcohols</i>		<i>Esters</i>	
Isobutanol	1.15	Ethyl acetate	1.08
<i>n</i> -Butanol	1.13	Ethyl carbonate	0.99
2-Octanol	1.13	<i>n</i> -Butyl acetate	0.97
Isoamyl alcohol	1.11	Ethyl <i>n</i> -butyrate	0.94
<i>n</i> -Pentanol	1.09	Ethyl isovalerate	0.88
<i>n</i> -Hexanol	1.06	Isoamyl <i>n</i> -butyrate	0.85
<i>n</i> -Heptanol	1.06	Ethyl <i>n</i> -nonylate	0.84
Cyclohexanol	1.04	Ethyl <i>n</i> -octanoate	
<i>n</i> -Octanol	1.03		
<i>Carboxylic acids</i>		<i>Ethers</i>	
Isovaleric acid	1.11	Diethyl ether	1.12
Heptanoic acid	1.04	Diisopropyl ether	1.01
Octanoic acid	1.03		
Undecylenic acid (25°C)	0.98	<i>Amines</i>	
Oleic acid	0.92	Di- <i>n</i> -propylamine	1.17
		Di- <i>n</i> -butylamine	1.06
		Aniline	0.98
<i>Aldehydes and ketones</i>			
Methyl <i>n</i> -hexyl ketone	1.08	<i>Nitriles</i>	
Methyl <i>n</i> -propyl ketone	1.07	Butyronitrile	1.00
Methyl <i>n</i> -butyl ketone	1.03	Isovaleronitrile	0.97
Monochloroacetone	1.00		
Methyl amyl ketone	0.99	<i>Nitro compounds</i>	
Ethyl <i>n</i> -propyl ketone	0.98	Nitromethane	0.97
<i>n</i> -Heptaldehyde	0.97	Nitrobenzene	0.81
1,1-Dichloroacetone	0.96	<i>o</i> -Nitrotoluene	0.79
Benzaldehyde	0.90	<i>m</i> -Nitrotoluene	0.97

Table VI—continued

Liquid	$\mu/\Phi$	Liquid	$\mu/\Phi$
<i>Alkanes</i>		Dichloromethane, methylene chloride	0.80
2,7-Dimethyloctane, diisooxyl	0.60	$\beta,\beta'$ -Dichlorodiethyl ether	0.78
2-Methylbutane, isopentane	0.59	Trichloromethane, chloroform	0.76
<i>n</i> -Pentane	0.58	1,2-Dibromomethane, ethylene dibromide	0.71
<i>n</i> -Hexane	0.55	1,1,2,2-Tetrabromoethane	0.70
<i>n</i> -Heptane	0.55	Tetrabromomethane, carbon tetrabromide	0.69
<i>n</i> -Octane	0.55	1,2,3-Tribromopropane	0.69
<i>n</i> -Decane	0.55	Tribromomethane, bromoform	0.67
Cyclohexane	0.55	Tetrachloromethane, carbon tetrachloride	0.61
Decahydronaphthalene, decalin	0.55	Diiodomethane, methylene iodide	0.61
<i>n</i> -Tetradecane	0.53	Tetrachloroethylene	0.59
Stanolax	0.51		
Liquid petroleum, Squibb	0.51	<i>Aromatic halogenated compounds</i>	
<i>Aromatic hydrocarbons</i>		Chlorobenzene	0.70
<i>p</i> -Cymene	0.73	Bromobenzene	0.69
Benzene	0.72	<i>o</i> -Chloronaphthalene	0.67
Toluene, methylbenzene	0.71	Iodobenzene	0.66
<i>o</i> -Xylene, 1,2-dimethylbenzene	0.71	<i>o</i> -Bromotoluene	0.66
<i>m</i> -Xylene, 1,3-dimethylbenzene	0.69	<i>o</i> -Bromonaphthalene	0.66
<i>p</i> -Xylene, 1,4-dimethylbenzene	0.69		
Ethyl benzene	0.69	<i>Fluorocarbon derivatives</i>	
Mesitylene, 1,3,5-trimethylbenzene	0.67	Perfluorotributylamine	0.95
		Perfluorodibutyl ether	0.55
<i>Aliphatic halogenated compounds</i>			
Isoamyl chloride	0.98	<i>Sulfur compounds</i>	
<i>t</i> -Butyl chloride	0.91	Ethyl mercaptan	0.85
Isobutyl chloride	0.88	Phenyl isothiocyanate	0.68
		Carbon disulfide	0.58



TABLE VII  
Interaction parameter  ${}^i\phi$  for mercury-nonmetallic liquid interfaces at 20°C.  
[Source: Girifalco and Good.<sup>17</sup>]

Liquid	${}^i\phi$	Liquid	${}^i\phi$
<i>Alcohols</i>			
Isobutanol	0.75	<i>n</i> -Hexane	0.62
<i>n</i> -Octanol	0.70	<i>n</i> -Heptane (25°C)	0.61
2-Octanol	0.69	<i>n</i> -Octane	0.60
<i>n</i> -Hexanol	0.59		
Isoamyl alcohol	0.58	<i>Aromatic hydrocarbons</i>	
<i>n</i> -Butanol	0.58	<i>m</i> -Xylene, 1,3-dimethylbenzene	0.63
<i>n</i> -Propanol	0.57	<i>p</i> -Xylene, 1,4-dimethylbenzene	0.62
Methanol	0.56	<i>o</i> -Xylene, 1,2-dimethylbenzene	0.61
Ethanol	0.53	Toluene, methylbenzene	0.61
		<i>n</i> -Propylbenzene	0.60
<i>Aliphatic acids</i>		<i>n</i> -Butylbenzene	0.60
Acetic acid, ethanoic acid	0.76	Benzene (25°C)	0.59
Valeric acid	0.76		
Oleic acid	0.75	<i>Aliphatic halogenated compounds</i>	
Undecylmic acid	0.64	Iodomethane, methyl iodide	0.84
		Iodoethane, ethyl iodide	0.79
<i>Ester</i>		1,2-Dichloroethane, ethylenedichloride	0.76
<i>n</i> -Butyl acetate	0.58	1,1-Dichloroethane, ethylidene chloride	0.76
		1,1,2,2-Tetrabromoethane	0.72
<i>Ether</i>		Dichloromethane	0.70
Diethyl ether	0.63	Trichloromethane, chloroform	0.64
		Tetrachloromethane, carbon tetrachloride	0.64
<i>Amines</i>		1,2-Dibromoethane, ethylene dibromide	0.59
Aniline	0.66		
Diisoumylamine	0.60	<i>Aromatic halogenated compounds</i>	
		Bromobenzene	0.62
<i>Nitro compounds</i>		Chlorobenzene	0.59
Nitroethane	0.82		
Nitrobenzene	0.59	<i>Sulfur compound</i>	
		Ethyl mercaptan	0.88
<i>Alkanes</i>		Water (25°C)	0.32
Isooctane	0.63		
<i>n</i> -Nonane	0.61		

Separation of dispersion and "polar" components of the surface free energy or cohesion parameters is important here, as emphasised by Wu.<sup>69</sup> The "optimum" wettability condition is when the "polar" (non-dispersive) components of the surface free energy are identical, and this is particularly important when the total surface energy of the two materials are comparable. (When the surface free energy of the liquid is much lower than that of the solid, complete wetting may still occur even though the polarities differ widely.)

For the selection of adhesives, both liquid–solid wetting and solid–solid adhesion are important factors, and both can be discussed in terms of cohesion parameters.<sup>7,15,16,55,69,116–125</sup> As on page 38, wetting is favoured by small  ${}^i\gamma$  and small  ${}^{is}\gamma$ . However, polymers which when liquid wet the substrate are not necessarily good adhesives: they must not crystallise, and there must be a matching of the cohesion parameters of the solids.

Adhesion performance can be assessed by simple swelling tests: the ideal bonding adhesive is one which exhibits a broad curve when the extent of swelling is plotted against solvent Hildebrand parameter, wide enough to overlap the Hildebrand parameters characterising both substrates. This can be achieved by using a copolymer formed from both high and low Hildebrand parameter monomers so that it is swollen by a wide range of polymers and is able to bond both poly(vinyl chloride) and rubber, for example.<sup>117</sup>

It is also useful to evaluate the work of adhesion in terms of partial surface free energies.

The work of adhesion of two solids,  $s$  and  $t$ , is

$${}^{st}W = {}^s\gamma + {}^t\gamma - {}^{st}\gamma. \quad (42)$$

Combining this with the solid–solid form of Eq. (6), for example, there results

$${}^{st}W \simeq 2[({}^s\gamma_d {}^t\gamma_d)^{1/2} + ({}^s\gamma_p {}^t\gamma_p)^{1/2}] \quad (43)$$

Similar expressions may be used for predicting if an adhesive  $st$  joint is stable in the presence of liquid  $i$ . For spontaneous separation

$${}^{st}\gamma > {}^{si}\gamma + {}^{ti}\gamma$$

The contribution of various factors to the work necessary to separate  $s$  from  $t$  have been considered by Schonhorn<sup>37</sup>. The dimensions of tensile strength are the same as those of cohesive pressure, and the ultimate strength of an ideal, flaw-free material is predicted to be about one-quarter of  $\delta^2$ .<sup>14–16</sup>

This provides a theoretical upper limit to the performance of polymeric adhesives:

$$\sigma = 0.25 {}^{st}\Phi^s \delta^s \delta \quad (44)$$

where  ${}^{st}\Phi$  is the interaction parameter or geometric mean correction factor.

From the discussion above it follows that an adhesive must have low  ${}^i\gamma$  and low  ${}^{is}\gamma$  for good wetting, but high  ${}^i\gamma$  and low  ${}^{is}\gamma$  for good adhesion. Therefore in

practice the surface free energy  $\gamma$  of an adhesive should be moderate, on the low side if good spreading is of critical importance, but high if great joint strength is desired. The surface free energies of polymeric adhesives are often modified by the incorporation of solvents, but again the ease of wetting may be accompanied by strain and discontinuities as solvents evaporate.

The adhesive strengths of surface coatings, as determined by a peel strength method, show a correlation with the cohesive pressure of the solvent from which the polymer film was cast. For a 10% lauryl methacrylate—90% methyl methacrylate copolymer on tin, the peel strength showed a fairly smooth curve as a function of cohesive pressure and a maximum of 400 MPa ( $\delta = 20 \text{ MPa}^{1/2}$ ).<sup>126</sup> The nature of coating solvent on film adhesion has applications in such areas as pharmaceutical tablets.<sup>127</sup> This correlation may be attributed to the state of the polymer in solution, best surface contact being achieved in a good solvent. A similar type of relationship was observed for the peeling of a poly(vinyl chloride) coating formed from an organosol on steel cleaned with different solvents.<sup>128</sup> This was interpreted as being due either to different cleaning actions of the solvents, or to solvent molecules remaining adsorbed on the metal surface and assisting the subsequent polymer adhesion.

In another typical application of Hildebrand parameters, a patent specification<sup>129</sup> states that a metal wire is plated with brass, copper or zinc, and then coated with a synthetic resin having a  $\delta$  value differing by less than  $2 \text{ MPa}^{1/2}$  from that of the rubber it is to be incorporated in as reinforcing. Other applications of cohesion parameters to adhesion include:

- relationship of the adhesion of photoresist film to the Hildebrand parameter of the solvent used to dissolve the film-forming agent<sup>130</sup>
- adhesion of lithographic materials<sup>113,131</sup>
- a surface free energy analysis of bioadhesion<sup>102,132</sup> and artificial blood substitutes<sup>110</sup>
- adhesive durability and fracture<sup>102</sup>
- adhesion of urethanes from oxypropylene polyols<sup>133</sup>
- bonding cold-curing denture base acrylic resin to acrylic resin teeth<sup>134</sup>
- compatibility of adhesives with Mylar® [poly(ethylene terephthalate)] and nylons<sup>118</sup>
- adhesion of Kevlar® aramid yarns to rubber<sup>135</sup>
- adhesive properties of polyepichlorohydrin<sup>136</sup>
- wettability and other adhesion properties of polysiloxanes<sup>28,137</sup>
- effect of solvent composition on the freezing resistance in storage of adhesives based on polychloroprene rubber<sup>138</sup>
- adhesive properties of methyl methacrylate-2,3-bis-(diorganophosphone) buta-1,3-diene copolymers<sup>139</sup>
- adhesion of organosols and plastisols to metal<sup>126,128,140</sup>

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