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# The Determination of Solubility Parameters of Solvents and Polymers by Means of Correlations with Other Physical Quantities

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## Synopsis

Correlations of solvent solubility parameters with molar attraction constants and with properties like surface tension, dipole moment, and index of refraction have been explored. From relations found to be valid for solvents, it is possible to calculate the solubility parameters for polymers. A relation between the dispersion contribution to the surface energy of polymers (a measurable quantity) and the dispersion solubility parameter of polymers has been found which is similar to a relation established for low molecular weight substances.

## INTRODUCTION

Predicting the energy of mixing of solvents and polymers from properties of the pure substances is an alluring prospect. In recent years, good progress has been made with methods based on the solubility parameter concept proposed by Hildebrand and others.[1] This theory relates the energy of mixing to the energies of vaporization of the pure components:

$$\frac{\Delta E_{\text{mix}}}{\phi_1\phi_2} = V_m(\delta_1 - \delta_2)^2$$
$$\delta = [C.E.D.]^{1/2} = \left[\frac{\Delta E_{\text{vap}}}{V_m}\right]^{1/2} \qquad (1)$$

where $\Delta E_{\text{mix}}$ = energy of mixing (or enthalpy, if $\Delta V_{\text{mix}}$ is zero), $\phi_1,\phi_2$ = volume fractions of the components, $V_m$ = average molar volume based on mole fractions, $\delta_1,\delta_2$ = solubility parameters, $C.E.D.$ = cohesive energy density, and $\Delta E_{\text{vap}}$ = energy of vaporization.

This theory has been developed for mixing of nonpolar substances. However, many of the solvents and polymers in common use are polar, i.e., have dipole moments and/or capabilities for hydrogen bonding. It is clear that these factors should be included in the theory.

The first step was made by Prausnitz et al.,[2,3] who divided the energy of vaporization into a nonpolar, dispersion part and a polar part. They were able to calculate a nonpolar solubility parameter $\lambda$ and a polar solubility parameter $\tau$. Hansen[4,5] divided the polar part $\tau$ into a dipole–dipole contribution and a hydrogen bonding contribution, both of which could be determined through solubility experiments with polymers. In this article, we will use the notation introduced by Hansen[4]):

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

where $\delta_d$ = solubility parameter due to dispersion forces, $\delta_p$ = solubility parameter due to dipole forces, and $\delta_h$ = solubility parameter due to hydrogen bonding (or in general due to donor–acceptor interactions).

Chen[6] showed that the contribution to the energy of mixing in polymer solutions caused by dispersion forces and dipole forces could be taken together to one enthalpy correction parameter $\chi_H$ (a Flory-Huggins-type correction parameter),

$$\chi_H = \frac{V_m}{RT}\left[(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2\right] \tag{3}$$

which, together with the $\delta_h$'s, could describe the solubility characteristics.

The two last-mentioned theories produce good predictions for the solubility of polymers.

The determination of the solubility parameters of many substances, however, is still a difficult and laborious undertaking. A new approach in recent literature has been to find correlations between solubility parameters $\delta(\delta_d, \delta_p, \delta_h)$ and other physical properties of the substance.

In this work we have explored possible correlations of the solubility parameters with molar attraction constants and with properties like surface tension, dipole moment, and index of refraction. Since it is obvious that not all contributions to molecular interactions affect both $\Delta E_{\text{vap}}$ and the physical properties mentioned in a parallel way, our main purpose was to improve existing relationships between them.

## RELATION BETWEEN SURFACE TENSION AND COHESIVE ENERGY DENSITY

Using a Lennard-Jones potential for the interaction between the molecules, one can derive[7]

$$\gamma_L = \left(1 - \frac{n_s}{n}\right)\frac{\epsilon}{a} \tag{4}$$

in which $\gamma_L$ = surface tension, $n_s$ = coordination number in the surface layer, $n$ = coordination number in the bulk phase, $a$ = cross-sectional area per molecule, and $\epsilon$ = minimum potential in a L-J potential curve. If the area per molecule is proportional to $V_m^{2/3}$, as for spherical molecules, and if $\Delta E_{\text{vap}}$ (= $V_m \cdot C.E.D.$) is proportional to $\epsilon$, the following relation holds

$$C.E.D. = A\left(\frac{1}{V_m}\right)^{1/3} \gamma_L \tag{5}$$

in which $A$ is a constant.

This relation has also been derived by some other approaches.[1,8,9,10] These derivations make use of a spherical symmetric type of potential around a molecule, in most cases explicitly a Lennard-Jones potential. This potential, however, is not valid for interactions between molecules in polar substances,[11] i.e.,

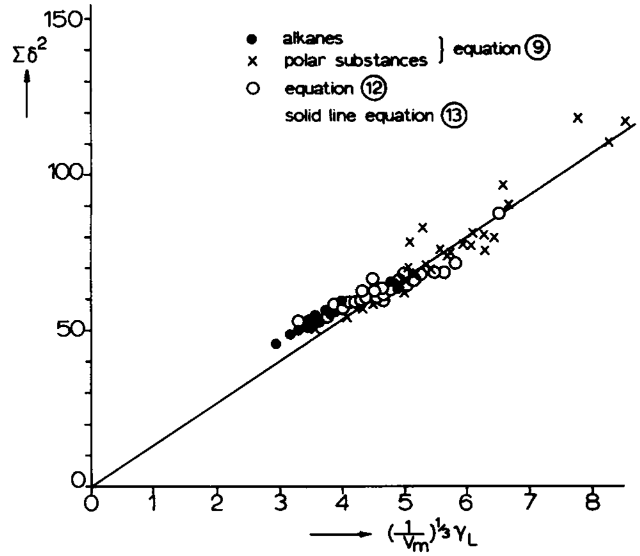

Fig. 1. Relation between surface tension and solubility parameters for solvents.

substances where dipole–dipole and hydrogen bonding forces act. Hence eq. (5) is found to be valid for *nonpolar liquids only.*

Beerbower[10] used the division of the different contributions to the *C.E.D.* according to Hansen[5] in a computer analysis and arrived at the following relationships, rewritten in the form of eq. (5):

$$\delta_d^2 + 0.632\,\delta_p^2 + 0.632\,\delta_h^2 = 13.9\left(\frac{1}{V_m}\right)^{1/3}\gamma_L \text{ for nonalcohols} \tag{6}$$

$$\delta_d^2 + \delta_p^2 + 0.06\,\delta_h^2 = 13.9\left(\frac{1}{V_m}\right)^{1/3}\gamma_L \text{ for most alcohols} \tag{7}$$

and

$$\delta_d^2 + 2\delta_p^2 + 0.481\,\delta_h^2 = 13.9\left(\frac{1}{V_m}\right)^{1/3}\gamma_L \text{ for acids, phenols and amines} \tag{8}$$

In our least-squares analysis of solvent data, we find that the relation

$$\delta_d^2 + \delta_p^2 = 13.8\left(\frac{1}{V_m}\right)^{1/3}\gamma_L \tag{9}$$

fits practically all substances listed in Table I, with a correlation coefficient of 0.99 and a standard error of estimate 5.6 for $\delta_d^2 + \delta_p^2$ (Fig. 1). Exceptions are some cyclic compounds, acetonitrile, carboxylic acids, and polyfunctional alcohols.

The reason for the absence of $\delta_h$ in this relationship, which is also valid for monofunctional hydrogen bonding substances, is probably the fact that the interactions responsible for liquid–vapor interfacial energy do not involve the breaking of hydrogen bonds; see also eq. (7).

Bagley et al.[11] showed recently that the contribution to the cohesive energy from hydrogen bonds depends on temperature only, at least at pressures not too far removed from atmospheric. The contributions of dispersion and dipolar forces are shown to be volume dependent.[11] When the vapor pressure at an

## TABLE I

Solubility Parameters, Surface Tensions, Molar Volumes, and Calculated Values of Solvents

| Substance | $\delta_d$[a] | $\delta_p$[a] | $\delta_h$[a] | $\gamma$[b] | $V_m$,[b] cc/mole | $(1/V_m)^{1/3}\gamma$ | $\delta_d^2 + \delta_p^2$ | CED = $\delta_d^2 + \delta_p^2 + \delta_h^2$ |
|---|---|---|---|---|---|---|---|---|
| Methanol | 7.42 | 6.0 | 10.9 | 22 | 40.7 | 6.39 | 91.1 | 204 |
| Ethanol | 7.73 | 4.3 | 9.5 | 22 | 58.5 | 5.67 | 78.2 | 168 |
| *n*-Propanol | 7.75 | 3.3 | 8.5 | 22.62 | 75.0 | 5.37 | 71.0 | 143.2 |
| *n*-Butanol | 7.81 | 2.8 | 7.7 | 23.38 | 91.8 | 5.19 | 68.8 | 122.1 |
| 2-Eth. butanol | 7.70 | 2.1 | 6.6 | 24.32 | 123.2 | 4.90 | 63.7 | 107.3 |
| Meth. isob. carb. | 7.47 | 1.6 | 6.0 | 22.63 | 127.2 | 4.51 | 58.4 | 94.4 |
| Cyclohexanol | 8.50 | 2.0 | 6.6 | 33.91 | 106.0 | 7.18 | 76.3 | 119.8 |
| 2-Butoxyethanol | 7.76 | 3.1 | 5.9 | 27.4 | 132 | 5.39 | 69.8 | 104.6 |
| Cellosolve | 7.85 | 4.5 | 7.0 | 28.2 | 97.8 | 6.13 | 81.9 | 130.9 |
| Diethylether | 7.05 | 1.4 | 2.5 | 16.50 | 104.8 | 3.51 | 51.7 | 57.9 |
| Furan | 8.70 | 0.9 | 2.6 | 23.38 | 72 | 5.63 | 76.4 | 83.3 |
| Diethyl sulfide | 8.25 | 1.5 | 1.0 | 24.5 | 108.2 | 5.15 | 70.3 | 71.3 |
| Dimethylsulfoxide | 9.00 | 8.0 | 5.0 | 42.86 | 71 | 10.37 | 145.0 | 170.0 |
| Acetone | 7.58 | 5.1 | 3.4 | 22.27 | 73.9 | 5.31 | 83.5 | 95.0 |
| Methyl ethyl ketone | 7.77 | 4.4 | 2.5 | 23.04 | 90.2 | 5.15 | 79.7 | 86.0 |
| Acetophenone | 8.55 | 4.2 | 1.8 | 37.72 | 117.1 | 7.72 | 90.7 | 94.0 |
| Tetrahydrofuran | 8.22 | 2.8 | 3.9 | 26.4 | 74.0 | 6.30 | 75.4 | 90.6 |
| Ethyl acetate | 7.44 | 2.6 | 4.5 | 22.99 | 98.5 | 4.99 | 62.1 | 82.4 |
| Acetonitrile | 7.50 | 8.8 | 3.0 | 27.55 | 52.9 | 7.35 | 133.7 | 142.7 |
| Butyronitrile | 7.50 | 6.1 | 2.5 | 25.84 | 87.0 | 5.85 | 93.5 | 99.7 |
| Nitromethane | 7.70 | 9.2 | 2.5 | 34.98 | 54.0 | 9.27 | 143.9 | 150.2 |
| Nitroethane | 7.80 | 7.6 | 2.2 | 32.13 | 71.3 | 7.76 | 118.6 | 123.4 |
| 2-Nitroprop. | 7.90 | 5.9 | 2.0 | 29.29 | 86.9 | 6.62 | 97.2 | 101.2 |
| Aniline | 9.53 | 2.5 | 5.0 | 42.79 | 91.1 | 9.52 | 97.1 | 122.1 |
| Nitrobenzene | 8.60 | 6.0 | 2.0 | 42.00 | 102.3 | 8.99 | 101.0 | 113.9 |
| Dimethylformamide | 8.52 | 6.7 | 5.5 | 35.2 | 77.0 | 8.29 | 117.5 | 147.1 |
| Diprop. amine | 7.50 | 0.7 | 2.0 | 22.28 | 136.9 | 4.33 | 56.7 | 60.7 |
| Diethylamine | 7.20 | 1.1 | 3.0 | 19.39 | 103.2 | 4.14 | 54.5 | 63.5 |
| Pyridine | 9.25 | 4.3 | 2.9 | 36.33 | 80.4 | 8.43 | 104.1 | 112.5 |
| Carbon tetrachloride | 8.65 | 0 | 0 | 26.15 | 97.1 | 5.70 | 74.8 | 74.8 |
| Chloroform | 8.65 | 1.5 | 2.8 | 26.53 | 80.7 | 6.15 | 77.1 | 84.9 |
| Trichloroethylene | 8.78 | 1.5 | 2.6 | 28.8 | 90.2 | 6.43 | 79.3 | 86.1 |
| Chlorobenzene | 9.28 | 2.1 | 1.0 | 31.37 | 102.1 | 6.72 | 90.5 | 91.5 |
| $\alpha$-Bromonaphthalene | 9.94 | 1.5 | 2.0 | 44.2 | 140.0 | 8.53 | 101.1 | 105.1 |
| Benzene | 8.95 | 0.5 | 1.0 | 28.18 | 89.4 | 6.31 | 80.4 | 84.1 |
| Toluene | 8.82 | 0.7 | 1.0 | 27.92 | 106.4 | 5.90 | 78.3 | 79.3 |
| Ethyl benzene | 8.70 | 0.3 | 0.7 | 28.48 | 123.1 | 5.73 | 75.8 | 76.3 |
| Hexane | 7.27 | 0 | 0 | 17.91 | 131.6 | 3.52 | 52.8 | 52.4 |
| Cyclohexane | 8.18 | 0 | 0 | 24.38 | 108.7 | 5.61 | 66.9 | 66.9 |
| Pentane | 7.05 | 0 | 0 | 15.48 | 116.104 | 3.17 | 49.7 | 49.7 |
| 3-Methylpentane | 7.13 | 0 | 0 | 17.60 | 130.611 | 3.47 | 50.8 | 50.8 |
| 3-Methylhexane | 7.29 | 0 | 0 | 19.30 | 146.714 | 3.66 | 53.1 | 53.1 |
| 2-Methylbutane | 6.75 | 0 | 0 | 14.46 | 117.38 | 2.95 | 45.6 | 45.6 |
| 2-Methylpentane | 7.13 | 0 | 0 | 16.87 | 132.875 | 3.31 | 50.8 | 50.8 |
| Heptane | 7.50 | 0 | 0 | 19.80 | 147.456 | 3.75 | 56.3 | 56.3 |
| Octane | 7.54 | 0 | 0 | 21.14 | 163.530 | 3.87 | 56.9 | 56.9 |
| Decane | 7.74 | 0 | 0 | 23.37 | 195.905 | 4.02 | 59.9 | 59.9 |
| Cyclopentane | 8.10 | 0 | 0 | 21.82 | 94.713 | 4.79 | 65.6 | 65.6 |
| Ethylcyclohexane | 7.96 | 0 | 0 | 25.14 | 143.141 | 4.81 | 63.4 | 63.4 |
| 2-Methylhexane | 7.22 | 0 | 0 | 18.80 | 148.576 | 3.33 | 52.1 | 52.1 |
| 2-Methylheptane | 7.34 | 0 | 0 | 20.14 | 164.607 | 3.67 | 53.9 | 53.9 |
| Acetic acid | 7.10 | 3.9 | 6.6 | 27.3 | 57.1 | 7.09 | 65.6 | 109.2 |
| Formic acid | 7.0 | 5.8 | 8.1 | 37 | 37.8 | 11.07 | 82.6 | 148.3 |
| Butyric acid | 7.30 | 2.0 | 5.2 | 26.6 | 92.5 | 5.88 | 57.3 | 84.3 |

[a] Hansen.[5,13]

[b] Riddick and Bunger.[36]

interface has moderate values, $\gamma_L$ therefore depends only on dispersion and dipolar forces. These forces also determine the internal pressure of a liquid[11] $P_i = \delta_d^2 + \delta_p^2$, so eq. (9) is in fact a relation between internal pressure and surface tension.

On the other hand, in the expression for the *C.E.D.* (*C.E.D.* $= \delta_d^2 + \delta_p^2 + \delta_h^2 = \Delta E_{\mathrm{vap}}/V_m$), $\delta_h$ cannot be omitted, since during evaporation of liquids toward dilute vapor, hydrogen bonds are being broken. Hence a relation between *C.E.D.* and $\gamma_L$, eq. (5), is not to be expected, unless $\delta_h = 0$.

Equation (9), of course, is not valid for polyfunctional alcohols which can from three-dimensional "networks" in bulk but not in the surface region. The other substances that deviate from eq. (9) have solubility parameters which are placed rather arbitrarily,[13] especially the carboxylic acids and cyclic compounds.

The $\delta$ parameters of cyclic molecules, being assessed by solubility experiments on polymers, are even more uncertain; these molecules "exhibit enhanced interaction affinity compared to flexible aliphatic molecules, because they act to separate the polymer chains and thus reduce interchain forces.[14]

In view of the uncertainties in the solubility parameters,* especially in $\delta_p$ and $\delta_h$, eq. (9) applied to all types of solvents is just as accurate in predicting $\gamma_L$ values as the three Beerbower relations (6)–(8) for separate series of solvents.

The contribution of the dispersion forces is nearly the same in both approaches; generally this contribution is the most important one.

Equation (9) is applicable to substances with zero $\delta_p$ values (hydrocarbons) and to those with finite $\delta_p$ and $\delta_h$ values (polar molecules). This suggest that relations of the form

$$\delta_d^2 = A\left(\frac{1}{V_m}\right)^{1/3}\gamma_L^d \tag{10}$$

where $\gamma_L^d$ = part of $\gamma_L$ due to dispersion forces, and

$$\delta_p^2 = A\left(\frac{1}{V_m}\right)^{1/3}\gamma_L^p \tag{11}$$

where $\gamma_L^p$ = part of $\gamma_L$ due to dipole forces, might be valid.

For a check of these relationships, $\gamma_L^d$ values have been determined by application of the homomorph concept: A homomorph is a hydrocarbon counterpart of the same size and shape, at the same reduced temperature $T_R = T/T_{\mathrm{critical}}$ ($T$ and $T_{\mathrm{cr}}$ in K).

From literature data on hydrocarbons,[15] a homomorph chart for $\gamma_L^d$ has been constructed (Fig. 2) which can be used for liquids that have simple linear saturated hydrocarbons as a homomorph. Knowing $V_m$ and $T_R$ of a substance, one can directly read $\gamma_L^d$ from Figure 2. In Table II, the $\gamma_L^d$ values found for several substances of this kind are shown, together with $\delta_d^2$ values obtained from recent homomorph charts for $\delta_d$.[3,16] The equation obtained by least-squares analysis of data from Table II is (Fig. 1)

$$\delta_d^2 = 13.2\left(\frac{1}{V_m}\right)^{1/3}\gamma_L^d \tag{12}$$

with a correlation coefficient 0.99 and standard error of estimate 3.5.

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* See for a discussion on this matter reference 16. We have used Hansen's tables unless otherwise stated.

TABLE II
Dispersion Solubility Parameter, Dispersion Contribution of Surface Tension, and Total Surface Tension of Solvents

| Substance | $\delta_d^2$ | $\gamma_L^d$, dyne/cm | $\gamma_L$, dyne/cm |
|---|---|---|---|
| Methanol | 60 | 16 | 22 |
| Ethanol | 60.4 | 17 | 22 |
| *n*-Propanol | 60.7 | 19 | 22.6 |
| *n*-Butanol | 60.7 | 20.5 | 23.4 |
| Pentanol-1 | 61.9 | 22.4 | 25.6 |
| Propylene glycol | 67.5 | 23 | 72 |
| Ethylene glycol | 71.2 | 22 | 46.5 |
| Butanediol-1,4 | 68.0 | 23.5 | 37.8 |
| Ethyl lactate | 62 | 22.5 | 28.8 |
| Butyl lactate | 61 | 24 | |
| Diethylene glycol | 63 | 21.5 | 48.5 |
| Dipropylene glycol | 68 | 25 | |
| 2-Butoxyethanol | 62.0 | 23 | 27.4 |
| Cellosolve | 62 | 21 | 28.2 |
| Diacetone alcohol | 63 | 23 | 31 |
| Methylcellosolve | 63 | 20.5 | |
| Diethyl ether | 52.5 | 15.5 | 16.5 |
| Methylal | 57 | 17 | 21 |
| Diethyl sulfide | 61 | 20.5 | 24.5 |
| Dimethylsulfoxide | 88.8 | 27 | 42.8 |
| Acetone | 59 | 18 | 22.3 |
| Methyl ethyl ketone | 59.3 | 19 | 23 |
| Ethyl acetate | 57.8 | 18.5 | 23.0 |
| Butyl acetate | 58.5 | 22 | 25 |
| Acetonitrile | 64.3 | 19 | 27.6 |
| Butyronitrile | 65.7 | 21.5 | 25.84 |
| Nitromethane | 67.6 | 20.5 | 34.9 |
| Nitroethane | 65.8 | 21.5 | 32.13 |
| Dimethylformamide | 69.7 | 24 | 35.2 |
| Dipropylamine | 57.5 | 20.5 | 22.7 |
| Diethylamine | 56 | 17.5 | 19.4 |
| Chlorobutane | 59 | 19.4 | |

In view of the fair agreement between the value of the numerical constant in equations (9) and (12), one can conclude that

$$\delta_d^2 + \delta_p^2 = A\left(\frac{1}{V_m}\right)^{1/3}\gamma_L \tag{13}$$

where A is about 13.5 and also

$$\gamma_L = \gamma_L^d + \gamma_L^p \text{ and } \gamma_L^h \approx 0 \tag{14}$$

for most substances.

Obviously, values of $\gamma_L^d$ calculated by Panzer[17] using

$$\gamma_L^d = 0.0715\, V_m^{1/3}\, \delta_d^2 \tag{15}$$

agree with values found in this work, when the error of estimates are taken into consideration. With the establishment of eq. (12) we have shown that this calculation of $\gamma_L^d$ is justified.

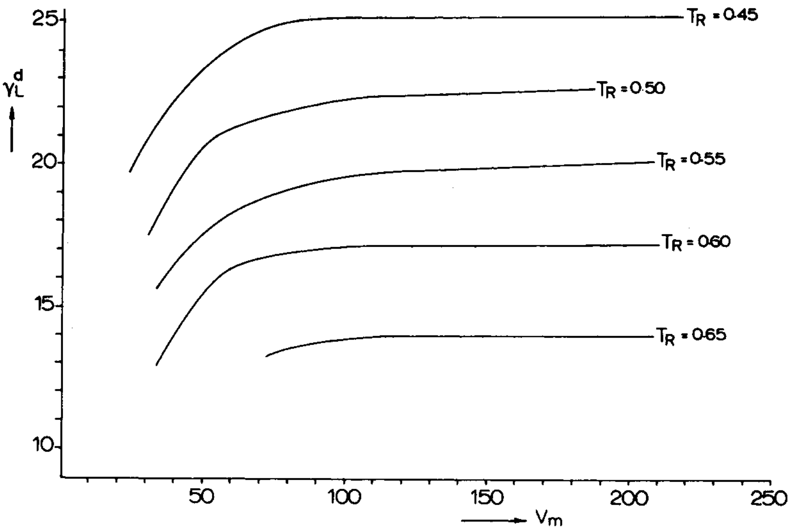


Fig. 2. Homomorph chart for determination of $\gamma_L{}^d$.

## CALCULATION OF THE DISPERSION CONTRIBUTION WITH MOLAR ATTRACTION CONSTANTS

From tables of molar attraction constants of characteristic groups in molecules,[18] it is possible to estimate the solubility parameter with the equation

$$\delta = \frac{\Sigma F_i}{V_m} \tag{16}$$

where $F_i$ = molar attraction constant of a specific group $i$. Since Hansen[4] has made a separation in contributions to the *C.E.D.*, one should expect the following relationships to hold:

$$\delta_d = \frac{\Sigma F_{id}}{V_m} \tag{17A}$$

$$\delta_p = \frac{\Sigma F_{ip}}{V_m} \tag{17B}$$

$$\delta_h = \frac{\Sigma F_{ih}}{V_m} \tag{17C}$$

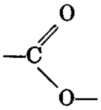
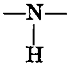
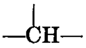
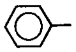
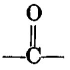
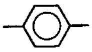
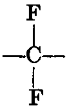
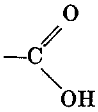
where $F_{id}$, $F_{ip}$, $F_{ih}$ are the molar attraction constants for dispersion-, dipole-, and hydrogen-bond forces, respectively.

### Dispersion Contribution $F_{id}$

We have derived the molar attraction constants for the dispersion contributions $F_{id}$ with the help of $\delta_d$ values taken from Hansen.[4,5] Results are given in Table III. The constants appear to be truly additive, within the errors inherent to the determination of $\delta_d$ values by the homomorph concept and by solubility experiments as performed by Hansen (up to 1 Hildebrand unit in $\delta_d$).[16]

TABLE III

Molar Attraction Constants (Dispersion Contribution) $F_{id}$

| Group | $F_{id}$, $\frac{\text{cal}\cdot\text{cc}^{1/2}}{\text{mole}}$ | Group | $F_{id}$, $\frac{\text{cal}^{1/2}\cdot\text{cc}^{1/2}}{\text{mole}}$ |
|---|---|---|---|
| $-CH_2-$ | 139 |  | 193 |
| $CH_3-$ | 201 |  $-\underset{\mathrm{H}}{\underset{\vert}{\mathrm{N}}}-$ | 70 |
| $-OH$ | 99 |  | 800 |
|  $-\overset{\vert}{\mathrm{C}}\mathrm{H}-$ | 51 |  | |
|  $-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}-$ | 159 |  | 738 |
| $-C\equiv N$ | 218 | | 659 |
| $-NO_2$ | 215 |  $-\overset{\mathrm{F}}{\overset{\vert}{\underset{\mathrm{F}}{\underset{\vert}{\mathrm{C}}}}}-$ | 160[a] |
|  | 200 | | |

[a] van Krevelen.[18]

## Polar Contribution $F_{ip}$

As an example of a polar group, the —OH alcohol group was chosen. The molar attraction constants calculated with $\delta_p$'s appear to be of constant magnitude when only one —OH group is present in the molecule. When two or more of these groups are present in the same molecule, the contribution of each —OH group to the attraction constant $F_{ip}$—(OH) decreases considerably (Table IV).

This, of course, can be expected to depend on the distance and mutual orientation of the groups. Therefore it is not possible to define molar attraction constants for dipole forces when more than one polar group is present in the molecule.

TABLE IV

Molar Attraction of One-OH Group (Polar Contribution) $F_{ip}$

| In substance | $F_{ip}$—OH, $\frac{\text{cal}^{1/2}\cdot\text{cc}^{1/2}}{\text{mole}}$ | |
|---|---|---|
| Methanol | 244 | av. 248 |
| Ethanol | 232 | |
| *n*-Propanol | 246 | |
| *n*-Butanol | 256 | |
| *n*-Pentanol | 248 | |
| 2-Ethylbutanol-1 | 259 | |
| 2-Ethylhexanol-1 | 251 | |
| 1,3-Butanediol | 218 | |
| Glycerol | 145 | |

### Contribution of H-Bonds $F_{ih}$

The energy of a special type of hydrogen bond $E_h$ can be taken as a constant,[19] which may be different for different H-bonded compounds. For the energy of one —OH group, Hansen[5,13] used 5000 cal/mole and he found

$$\delta_h = \sqrt{E_h \cdot A/V_m} = \sqrt{5000\,A/V_m} \tag{18}$$

where $A$ is the number of —OH groups in the molecule. Since $\Sigma F_{ih} = V_m\,\delta_h = \sqrt{V_m\,5000\,A}$, the molar attraction constant $F_{ih}$ for a H-bonding group in a homologous series would depend on molar volume, which makes H-bonding contributions to $F_i$ intractable. Equation (18) can be used, however, if the energies for different types of H bonds or acceptor/donor complexes are known.[20]

We can conclude from this section that (a) the molar dispersion attraction constants $F_{i,d}$ (Table III) enable one to calculate $\delta_d$ for liquids and polymers; (b) since constant values for $F_{i,p}$ and $F_{i,h}$ cannot be defined, the prediction of the total solubility parameter $\delta$ from attraction constant contributions is of limited value.

## RELATION BETWEEN INDEX OF REFRACTION ($n_D$) AND $\delta_d$

Sewell[21] has already searched for a relationship between the *C.E.D.* and the index of refraction. The main idea is that the interaction energy between nonpolar molecules is dependent on the polarizability (London dispersion forces). The polarizability can, on the other hand, be described by the Lorentz-Lorentz equation:

$$\frac{4}{3}\pi N/V\,\alpha = \frac{n_D^2 - 1}{n_D^2 + 2} \tag{19}$$

where $n_D$ = refractive index, $N$ = number of molecules per cc, and $\alpha$ = average polarisability per molecule.

Sewell found a correlation between the *C.E.D.* and $(n_D^2 - 1)/(n_D^2 + 2)$ with *C.E.D.* values calculated from Small's tables.[18,28] Using the separation of *C.E.D.* in three contributions, we expect a relationship between $\delta_d$ and $n_D$ even for polar substances, in which relation the interference of polar and hydrogen bonding forces has vanished.

The right-hand side of eq. (19) is almost a linear function of $n_D$ in the region of $n_D$ values observed ($n_D$ between 1.3 and 1.6). This is also true for $n_D^2$ (see Fig. 3) and therefore one of these functions can be used with equivalent results. The relation found to be valid here for the substances of Table V is

$$\delta_d = 9.55 n_D - 5.55 \tag{20}$$

with correlation coefficient 0.90 and standard error of estimate 0.32. This relation resembles very much the relationships found by Papazian[22] and by Holmes[23] between the surface tension and the dielectric constant or the square of the index of refraction.

Equation (13) suggests that a factor $V_m^{1/6}$ might occur in eq. (20). This dependence on $V_m$ has not been evaluated in this study because of the minor importance of this factor in the range of molar volumes studied. For more accurate studies, however, incorporation of this dependence of $V_m$ might be recommendable.

TABLE V

Index of Refraction, Dipole Moment, and Related Solubility Parameters for Solvents

| Substance | Index of refraction $n_D$[a] | Dispersion solubility par. $\delta_d$[b] | Dipole moment $\mu$ (D)[c] | Polar solubility par. $\delta_p$[d] |
|---|---|---|---|---|
| Methanol | 1.32840 | 7.42 | 1.70 | 6.0 |
| Ethanol, 99.9% | 1.36140 | 7.73 | 1.69 | 4.3 |
| *n*-Propanol | 1.38556 | 7.75 | 1.68 | 3.3 |
| *n*-Butanol | 1.3993 | 7.81 | 1.66 | 2.8 |
| Pentanol-1 | 1.4100 | 7.81 | 1.7 | 2.2 |
| Propylene glycol | 1.4329 | 8.24 | 2.25 | 4.6 |
| Ethylene glycol | 1.4318 | 8.25 | 2.28 | 5.4 |
| Cyclohexanol | 1.46477 | 8.50 | 1.86 | 2.0 |
| Ethyl lactate | 1.4124 | 7.80 | 2.4 | 3.7 |
| 2-Butoxyethanol | 1.41980 | 7.76 | 2.08 | 3.1 |
| Oxitol (Cellosolve) | 1.4077 | 7.85 | 2.08 | 4.5 |
| Diacetone alcohol | 1.4235 | 7.65 | 3.24 | 4.0 |
| Diethyl ether | 1.35243 | 7.05 | 1.15 | 1.4 |
| Furan | 1.42140 | 8.43 | 0.71 | 0.9 |
| Dioxane | 1.42241 | 8.55 | 0.45 | 0.9 |
| Methylal | 1.35335 | 7.35 | 0.74 | 0.9 |
| Carbon disulfide | 1.62799 | 9.97 | 0.06 | 0 |
| Dimethylsulfoxide | 1.4783 | 9.00 | 3.9 | 8 |
| $\gamma$-Butyrolactone | 1.4348 | 9.26 | 4.12 | 8.1 |
| Acetone | 1.35868 | 7.58 | 2.69 | 5.1 |
| Acetophenone | 1.53423 | 8.55 | 2.69 | 4.2 |
| Tetrahydrofuran | 1.40716 | 8.22 | 1.75 | 2.8 |
| Ethyl acetate | 1.37239 | 7.44 | 1.88 | 2.6 |
| *n*-Butal acetate | 1.3900 | 7.67 | 1.84 | 1.8 |
| Isoamyl acetate | 1.4007 | 7.45 | 1.82 | 1.5 |
| Acetonitrile | 1.34411 | 7.50 | 3.44 | 8.8 |
| Butyronitrile | 1.3838 | 7.50 | 3.57 | 6.1 |
| Nitromethane | 1.38118 | 7.70 | 3.56 | 9.2 |
| Nitroethane | 1.39193 | 7.80 | 3.60 | 7.6 |
| 2-Nitropropane | 1.39439 | 7.90 | 3.73 | 5.9 |
| Aniline | 1.58628 | 9.53 | 1.51 | 6.0 |
| Nitrobenzene | 1.5500 | 8.60 | 4.03 | 6.0 |
| Dimethylformamide | 1.43047 | 8.52 | 3.86 | 6.7 |
| Dipropylamine | 1.4043 | 7.50 | 1.03 | 0.7 |
| Diethylamine | 1.3854 | 7.30 | 1.11 | 1.1 |
| Morpholine | 1.4542 | 8.89 | 1.50 | 2.4 |
| Cyclohexylamine | 1.45926 | 8.35 | 1.26 | 1.5 |
| Pyridine | 1.51016 | 9.25 | 2.37 | 4.3 |
| Carbon tetrachloride | 1.4600 | 8.65 | 0 | 0 |
| Chloroform | 1.4460 | 8.65 | 1.15 | 1.5 |
| Ethylene chloride | 1.4448 | 8.50 | 1.86 | 2.6 |
| Methylene chloride | 1.42416 | 8.52 | 1.14 | 3.1 |
| 1-1,1-Trichloroethane | 1.4379 | 8.25 | 1.57 | 2.1 |
| 1-Chlorobutane | 1.4021 | 7.95 | 1.90 | 2.7 |
| Trichloroethylene | 1.4767 | 8.78 | 0.8 | 1.5 |
| Chlorobenzene | 1.52481 | 9.28 | 1.54 | 2.1 |
| *o*-Dichlorobenzene | 1.55145 | 9.35 | 2.27 | 3.1 |
| $\alpha$-Bromonaphthaline | 1.6580 | 9.94 | 1.29 | 1.5 |
| Benzene | 1.50112 | 8.95 | 0 | 0.5 |
| Toluene | 1.49693 | 8.82 | 0.31 | 0.7 |
| Xylene | 1.49722 | 8.65 | 0.45 | 0.5 |

(*continued*)

TABLE V (*continued*)

| Substance | Index of refraction $n_D$[a] | Dispersion solubility par. $\delta_d$[b] | Dipole moment $\mu$ $(D)$[c] | Polar solubility par. $\delta_p$[d] |
|---|---|---|---|---|
| Ethylbenzene | 1.49588 | 8.70 | 0.37 | 0.3 |
| Styrene | 1.54682 | 9.07 | 0.13 | 0.5 |
| Tetralin | 1.54135 | 9.35 | 0.60 | 1.0 |
| Hexane | 1.37486 | 7.24 | 0.085 | 0 |
| Cyclohexane | 1.426223 | 8.18 | 0 | 0 |
| Acetic acid | 1.3719 | 7.10 | 1.68 | 3.9 |
| Formic acid | 1.37140 | 7.00 | 1.82 | 5.8 |
| Butyric acid | 1.3980 | 7.30 | 1.65 | 2.0 |
| Benzaldehyde | 1.5455 | 9.15 | 2.77 | 4.2 |

[a] Values from Riddick and Bunger[36] and *Handbook of Chemistry and Physics*.[37]

[b] Values from Hansen.[5,13]

[c] Values from Riddick and Bunger[36] and McClellan.[26]

[d] Values from Hansen.[5,13]

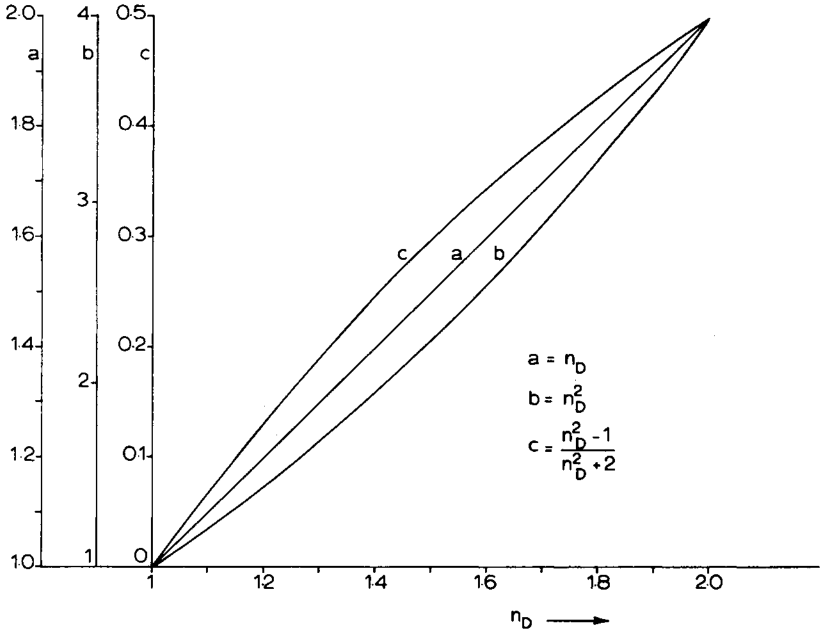


Fig. 3. Some functions of $n_D$.

## RELATION BETWEEN THE DIPOLE MOMENT ($\mu$) AND $\delta_p$

In order to calculate the contribution of permanent dipoles to the cohesive energy density, Hansen[5] has used the formula proposed by Böttcher[24]:

$$\delta_p^2 = \frac{12108}{V_m^2}\,\frac{\epsilon - 1}{2\epsilon + n_D^2}\,(n_D^2 + 2)\mu^2 \tag{21}$$

where $\epsilon$ = dielectric constant and $\mu$ = dipole moment.

Another, and more simple empirical relationship has been proposed by Beerbower:[16]

$$\delta_p = A' \frac{\mu}{V_m^{1/2}}. \tag{22}$$

When the statistical thermodynamical derivation of Bonn and van Aartsen[9] is used, including the Keesom potential for dipole–dipole interaction (which in fact is not justified),[12] the following relation can be found:

$$\delta_p = A'' \frac{\mu^2}{V_m^{3/2}}. \tag{23}$$

Empirically we found a linear relationship between $\delta_p$ and the square root of the right-hand side of eq. (23):

$$\delta_p = A''' \frac{\mu}{V_m^{3/4}} \tag{24}$$

When $\delta_p$ values are taken from Hansen,[5,14] we found for 59 solvents (Table V)

$$\delta_p = 50.1 \frac{\mu}{V_m^{3/4}} \tag{24a}$$

with a correlation coefficient 0.99 and a standard error of estimate 0.38. For the relation of Beerbower, eq. (22), these solvents give

$$\delta_p = 9.5 \frac{\mu}{V_m^{1/2}} \tag{22a}$$

with a correlation coefficient 0.97 and a standard error of estimate 0.50. We may conclude here that either of the relations (24a) or (22a) can be used to calculate $\delta_p$ values.

## APPLICATION TO POLYMERIC SYSTEMS

Applying the relations found in the preceeding sections to polymeric system[S] we have been able to predict $\delta_d$ values for polymers from $n_D$ and $F_{td}$ data, respectively. If the dipole moment of the polymer is known, we are able to predict $\delta_p$ of the polymer also. Furthermore, since a particular type of hydrogen bond appears to have a constant energy, we can calculate $\delta_h$ from this energy and the molar volume of a segment, using eq. 18.

### Dispersion Contribution to the *C.E.D.* for Polymers from $F_{td}$ and $n_D$

In Table VI, the $\delta_d$ values for several polymers are given, calculated from $F_{td}$, eq. (17a), and from $n_D$, eq. (20). As can be seen from the table, $\delta_d$ values for polymers with polar groups attached to the phenylene ring like in poly(2,6-dimethyl-1,4-phenylene oxide) have not been included in the calculations from $F_{td}$. There were not enough $\delta_d$ values of low molecular weight analogs available to incorporate the effect of the phenylene ring on the additive value $F_{td}$ for an attached polar group. A shift to somewhat higher $F_{td}$ values is expected, as is the case for the additive constants for the molar refraction ($R$), calculated by Goedhart.[25]

TABLE VI
Solubility Parameters and Other Physical Properties of Polymers

| Polymer | $n_D$ | $\mu(D)$ | $V_{m_s}$ | $\gamma^d_s$ | $\delta_d$ from $F_{id}$, eq. (17a) | $\delta_d$ from $n_D$, eq. (20) | $\delta_p$ from $\mu$, eq. (24a) | $\delta_h$ from eqs. (18), (27) |
|---|---|---|---|---|---|---|---|---|
| Polyethylene | 1.483 | 0[c] | 32.8 | 35 | 8.47 | 8.61 | 0 | 0 |
| Polystyrene | 1.591 | 0.26[c] | 99 | 44 | 9.37 | 9.64 | 0.42 | 1.0 |
| Poly(tetrafluoroethylene) | 1.298[a] | 0[d] | 50 | 19.5 | 6.2 | 6.84 | 0 | 0 |
| Polyacrylonitrile | 1.514 | 2.75[d] | 44.8 | — | 9.11 | 8.91 | 7.9 | 3.3 |
| Poly(2,6-dimethyl-1,4-phenylene oxide) | 1.567 | 0.88[d] | 111.7 | — | — | 9.41 | 1.3 | 2.4 |
| Poly(methyl methacrylate) | 1.490 | 1.30–1.90[c] | 85.6 | 50.5[b] | 8.57 | 8.68 | ±2.8 | 3.8 |
| Nylon 6.6 | 1.530 | 2.8[d] | 211.5 | — | — | 9.06 | 2.5 | 6.0 |
| Poly(vinyl chloride) | 1.539 | 1.67–1.75[c] | 45.1 | — | — | 9.15 | 4.9 | 1.5 |
| Poly(ethylene terephthalate) | 1.580 | 1.44[d] | 144.5 | 53[b] | — | 9.54 | 1.7 | 4.2 |

[a] Calculated with additive constants from molar refraction as proposed by Goedhart.[23]

[b] Private communication, Bargeman.[34]

[c] From McClellan.[24]

[d] Estimated: 80% of corresponding monomer value.

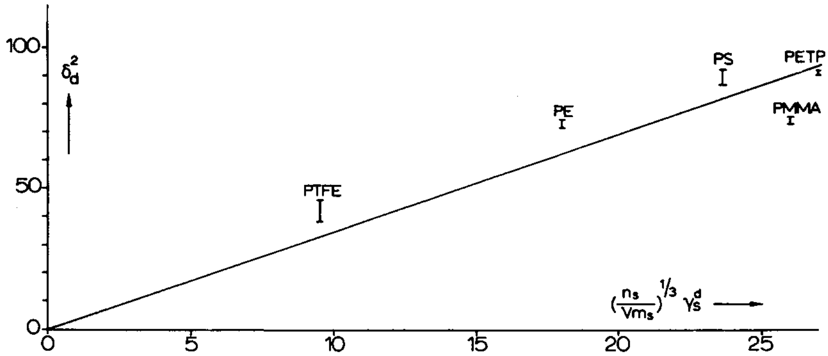


Fig. 4. Relation between dispersion part of the surface tension and the solubility parameters for polymers.

## Relation Between $\delta_d^2$ and $\gamma_s^d$ for Polymers

In the case of polymers, the molar volume derivations based on spherical molecules are not valid, and therefore one cannot use the factor $(1/V_m)^{1/3}$ from eq. (5). Wu[27] has proposed an approach for polymers in which he used an effective cross-sectional area to obtain the factor between the *C.E.D.*, calculated with attractive constants,[28] and the $\gamma_c$ value of Zisman.[29] Equation (5) then becomes

$$C.E.D._s = A \left(\frac{n_s}{V_{ms}}\right)^{1/3} \gamma_c \tag{25}$$

where $C.E.D._s = C.E.D.$ of a segment, $V_{ms} = V_m$ of a segment, and $n_s$ = number of atoms in a segment.

The *C.E.D.* values calculated by Wu, using the attractive constants of Small,[28] do not represent true dispersion contributions; neither are the values of the critical surface tensions for polar polymers based on dispersion contributions.[30] Therefore, the relation we propose for polymers must be analogous to eq. (10) and reads

$$\delta_d^2 = A \left(\frac{n_s}{V_{ms}}\right)^{1/3} \gamma_s^d \tag{26}$$

where $\gamma_s^d$ is the dispersion contribution part of the free surface energy of the polymer. Values of $\gamma_s^d$ are known for nonpolar polymers,[31] and in two cases immersion calorimetry has been performed on polar polymers to obtain $\lambda_s^d$ values.[34]

In Figure 4, a graphic representation of eq. (26) is given, where values of Table VI have been used. The constant $A$ found by least-squares fitting has the value 3.4; because of a different geometric factor, this constant deviates from the one found in eq. (12). The correlation is good, but more data are necessary and we hope that they will become available soon.

## Polar Contribution to the *C.E.D.* for Polymers, $\delta_p$

The measured average dipole moments of polymers[26] are generally 70–90% of the dipole moments of the corresponding monomer unit. For polymer $\mu$ values not to be found in the literature, we have estimated the dipole moment at 80% of the dipole moment of the monomer.

The $\delta_p$'s calculated with eq. (24a) are given in Table VI.

## The Hydrogen-Bonding Parameter $\delta_h$ for Polymers

It is argued above that the energy for a hydrogen bond should be known in order to make an estimate of $\delta_h$. The energy for the H bond in alcohols has been given as 5 kcal/mole. For the energy of the amide H bond, we have used the value of 3.9 kcal/mole given by Pimentel and McClellan.[19]

For esters, nitriles, monochloro, ether, and cyclic compounds, we have used values of $E_h$ compiled by Beerbower and Hansen:[20]

$$E_h = \delta_h^2 V_m \tag{27}$$

$E_h$ = enthalpy of an H bond or donor/acceptor group

| | |
|---|---|
| —ester group | about 1250 cal/mole |
| —nitrile group | about 500 cal/mole |
| —ether group | about 550 cal/mole |
| —monochloro substituent | about 100 cal/mole |
| —phenylene ring | about 100 cal/mole |

The results of calculations of $\delta_h$ for some polymers, using the above $E_h$ values of H bond types are given in Table VI.

## DISCUSSION

In the foregoing sections, we have discussed relations between solubility parameters and other physical properties, and the possibility of determining the solubility parameters with additive constants. From the relations established, it is possible to determine the solubility parameters ($\delta_p$, $\delta_d$, $\delta_h$) for solvents and polymers. Especially for the latter group of substances, this is a very important result, because otherwise time-consuming determinations (solubility or swelling experiments) must be made.

We have demonstrated that only the dispersion contribution to the *C.E.D.* can be calculated with a molar attraction constant. The values of $F_{id}$ which we found for —$CH_3$ and —$CH_2$— equal those reported by Allen, Gee, and Wilson[32] for *n*-alkanes. The value of $\delta_d$ for polyethylene calculated with these values also compare quite well with the value obtained by extrapolation of the $\delta_d$ of *n*-alkanes to infinite chain length.[32] The literature values for $F_i$[18] used in the calculation of the total solubility parameter always represent some kind of compromise, especially when hydrogen bonds occur. The solubility parameters calculated with these values can be considered as highly approximate only. For nonpolar substances, these $\delta$ values are apparently too low. Our solubility parameter components ($\delta_d$, $\delta_p$, $\delta_h$) for polymers have been calculated from relationships based on solvent data of Hansen. Therefore, it is better to compare our values with his.[33]

This is possible by making plots of solubility spheres similar to those Hansen used to obtain his values. Because $\delta_d$ values especially cover only a narrow range ($\delta_d \approx 7$–$10$), the solubility spheres are usually occupied only for a small part by coordinates ($\delta_d$, $\delta_p$, $\delta_h$) of solvent solubility parameters. It is therefore possible to envelope these points by a solubility sphere with different center coordinates ($\delta_d$, $\delta_p$, $\delta_h$ of the polymer) and a different radius. When the radius increases, the center coordinates must shift in the direction of the empty part of the solubility sphere.

Although the polymer solubility parameters given by Hansen[33] can therefore be only approximate, his method of plotting can be used to check polymer $\delta$ values obtained in different ways: these values have to be the center of a solubility sphere which envelopes the coordinates of the solvents in which the polymer is soluble, and which excludes the coordinates of the nonsolvents. The values given in Table VI satisfy this condition.

The difference between $\delta_d$ from $F_{id}$ and from $n_D$ in Table VI is within the confidence limit of twice the standard error of estimate ($\sim$0.6 Hildebrand).

Although solubility parameters are a very helpful instrument to estimate polymer swelling and solubility, it should be emphasized that they reflect the attractive forces in the pure substances only. Interactions not expected by combining separate $\delta$-parameter values may arise, especially so for hydrogen bonds.

Chen[6] has shown that upon mixing, the dispersion and dipolar forces can be taken together to one parameter $\chi_H$ and that the hydrogen-bonding forces need to be taken into consideration separately. Donor–acceptor complexes are known to be formed when an electron donor group can come into contact with an acceptor group. In a pure substance which is of electron-donating type, $\delta_h$ may be small. When, however, this substance is mixed with a substance which is electron accepting (also $\delta_h$ small), strong hydrogen bonds will be the result.

We feel that these shortcomings of the solubility parameter theory can be overcome if it becomes possible to extend Drago's[35] theory for the prediction of the enthalpy of donor–acceptor complexes to solvent and polymer–solvent mixtures.

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