The Molecular Factors Affecting The Solubility Parameter

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Synopsis

A study of the solubility parameter δ^2 was pursued in order to obtain further information on the prominent molecular factors affecting its value. The details of the expressions derived for the components of δ^2 depends on the considerable usage of both classical statistical thermodynamics and the well-known equations for intermolecular forces. The results confirm that relatively simple expressions for the components of δ^2 are found. The disperson component of the solubility parameter, δ_d^2, is a function of the molecular polarizability, fractional polarity, molar volume, and van der Waals volume. The polar component of the solubility parameter, δ_p^2, is a function of the dipole moment, temperature, molar volume, and van der Waals volume; δ_d^2 is found to increase linearly with molecular size, while δ_p^2 is found to decrease with molecular size (except at low molecular volumes). As will be shown, the expressions derived here have considerable utility in elucidating results obtained by other researchers.

INTRODUCTION

The solubility parameter δ^2, defined as the square root of the cohesive energy density (ratio of the energy of vaporization, ΔE_v, to the molar volume) is used extensively in the field of polymer science.[1-12] (It should be noted that the cohesive energy density is a measure of the magnitude of the intermolecular forces within a liquid.) For example, considerable use of δ, in both theoretical and experimental solution studies, is found in the scientific literature.[4] Initially, Scatschard and Hildebrand[2] formulated the δ concept in their theories of the mixing of nonpolar substances. Subequently, polar and hydrogen bonding factors were included into δ.[5,11,13-16] In time, relationships were found to exist between δ and such physical quantities as the tensile strength of unoriented polymers, surface free energy, and the glass transition temperature, to cite a few examples.[3,17,18]

The ability to estimate δ would be quite useful. Thus, several methods[19-24] have been developed for its evaluation; δ can be directly determined experimentally from low molecular weight liquids of high volatility using ΔE_v at a given temperature. The molar volume of liquid, V_l, is normally calculated from known values of density and molecular weight. In high molecular weight polymers, where extremely low volatility is found, indirect methods are used. Small[19] has pointed out that the so-called molar attraction constants $(E_v V_l)^{0.5}$ were additive constants for organic functional groups. From these constants δ can be determined. This method has enjoyed widespread use. It has been noted[20] that these molar attraction constants would be more accurate if chain length corrections were made.

Swelling of a crosslinked polymer utilizing a series of solvents of differing δ

has also been proved effective in determining δ of the polymer if possible polar effects are ignored.[22]   Each solvent will swell the polymer by a certain amount. The extent of the swelling is dependent upon how closely the solubility parameters of the two materials match.   A maximum is observed when the amount of swelling versus solvent δ is graphed.   This maximum is assumed to occur when the solvent δ equals that of the polymer.   A method analogous to solvent swelling involves the measurement of the intrinsic viscosity of the polymer solution as a function of solvent δ.[22]   The maximum in the intrinsic viscosity curve again corresponds to the polymer's δ.   Other experimental methods[22] have been devised in order to find the δ of a polymeric material, including swelling in conjugation with stress–strain measurements.   Huglin and Pass[22] applied these methods to the determination of the cohesive energy density of polytetrahydrofuran with excellent agreement.   Finally Koenhin and Smolders[23] have shown that it is possible to determine δ of polymers by means of correlations with such physical quantities as surface tension, index of refraction, and dipole moment.

In this work statistical thermodynamics[24,25] combined with the equations for the various contributions to intermolecular forces[26] leads to expressions relating δ with known molecular parameters.   It is the author's hope that this will lead to an improved understanding of the factors affecting a solvent's or polymer's δ and its relationship with other physical properties.

THEORY

The key to the establishment of the major molecular parameters that contribute to the solubility parameter involve the use of classical statistical thermodynamics of the liquid state[25] and the equations describing the interaction energies between molecular species.   As noted by Hill,[25] approximate theories for the liquid state are generally used because of the difficulty in treating an extremely large number of individual particles.   In this case a theory of the liquid state[25] is used in which we restrict ourselves with pairwise additive potential energy.   The discussion will begin with a brief thermodynamic analysis of the gas phase.   This phase exists due to the varporization of the liquid phase.

The canonical ensemble partition function Q_g for molecules of a gas that are independent and indistinguishable from each other can be expressed as a function of Planck's constant h, the mass of the individual molecule m, the Boltzmann constant k, temperature T, the volume v, and the number of molecules N[25]:

$$Q_g = q_g^N/N! \qquad q_g = V/\Lambda^3 \tag{1a}$$

where

$$\Lambda = h/(2\pi m k T)^{0.5} \tag{1b}$$

The above equations are the well-known expressions used in dealing with an ideal gas.   The partition function q_g pertains to a molecule moving in a potential free volume.

To be realistic in the model of the liquid state, we should assume that the molecules do interact with each other through their intermolecular forces.   Each molecule moves in a uniform potential field provided by the other randomly oriented molecules.   Therefore, two modifications in q_l (partition function for

the liquid state) have to be made, both of which arises from intermolecular forces.[25] The first consideration is due to the finite size of molecules, which eliminates some volume for an individual molecule to transverse through. Therefore, V in eq. (1) should be replaced with a so-called free volume V_F. Secondly, the Boltzmann factor should be included ($e^{-\phi/2kT}$) in order to represent the intermolecular potential field that each molecule is transversing. The potential energy of interaction between any molecule and its surroundings is represented by ϕ. One can then write the following expressions for the partition function of the liquid, Q_l:

$$Q_l = q_l^N/N! \qquad q_l = V_F e^{-\phi/2kT}/\Lambda^3 \tag{2}$$

The free volume is essentially the amount of volume that molecules can travel through. The volume excluded to other molecules arises from intermolecular pair interactions. Normally, one writes the following[25] approximate expression for V_F:

$$V_F = V - Nb \qquad b = 2\pi r^{*3}/3 \tag{3}$$

where r^* is the equilibrium distance between two molecules measured at the minimum in potential energy. The explicit expression[25] for the potential of interaction, ϕ, for a molecule surrounded by other molecules is given by eq. (4):

$$\phi = - \int_{r^*}^{\infty} \mu(r) \frac{N}{V} 4\pi r^2 dr \tag{4}$$

where $\mu(r)$ is the potential energy between pairs of molecules which is a function of intermolecular distance r. Several equations[26] for $\mu(r)$ can generally be used; included are the Lennard–Jones potential (LJP), eq. (5), and the Sutherland potential (SP), eq. (6):

$$\mu(r) = 4\epsilon^* \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \tag{5}$$

$$\mu(r) = -\epsilon^*/r^6 \qquad \text{for } r > \sigma$$

$$\mu(r) = \infty \qquad \text{for } r < \sigma \tag{6}$$

where ϵ^* is the energy of intermolecular interaction between two molecules at the equilibrium distance r^* and σ is the van der Waals radius.

Expressions for the potential energy of the molecular interaction, ϕ, can be obtained by substituting eqs. (5) or (6) into eq. (4) and performing the integration. These results, utilizing both the LJP and SP, are found to be quite similar in form except for a constant:

$$\phi_{SP} = - \frac{4}{3} \pi (N/V_l) \epsilon^* r^{*3} \tag{7}$$

$$\phi_{LJP} = - \frac{32}{9} \pi (N/V_l) \epsilon^* r^{*3} \tag{8}$$

The important point to note here is that the expression used for $\mu(r)$ is not sensitive to the final result in the calculation of ϕ. For our purposes, eqs. (7) and (8) can be summarized by the following expression:

$$\phi = -C\pi (N/V_l) \epsilon^* r^{*3} \tag{9}$$

With the information gathered so far it is possible to obtain an equation for the energy of both the gaseous and the liquid states. The difference in energy between the gas and liquid states ($\Delta E = E_l - E_g$) is the quantity of interest in this work because of its direct proportionality with the solubility parameter. As stated previously, the molar cohesive energy of a liquid is the energy needed to break all of the intermolecular contacts. One assumes that in the gas phase there are no interactions between molecules. In essence the gas molecules behave as an ideal gas, i.e., negligible potential energy. The energy of both phases can now be calculated from classical statistical thermodynamics[25]:

$$E = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N_1 V} \tag{10}$$

The necessary substitutions and mathematical treatment are straightforward. The energy change ΔE for both the LJP and SP are given in the following expressions:

$$\Delta E_{\text{LJP}} = \frac{16}{9} \pi \epsilon^* (N^2/V_l) r^{*3} \tag{11}$$

$$\Delta E_{\text{SP}} = \frac{2}{3} \pi \epsilon^* (N^2/V_l) r^{*3} \tag{12}$$

In the general case, the cohesive energy density is defined in terms of ΔE which lead directly to the appropriate expression needed to describe δ^2:

$$\delta^2 = C' \pi \epsilon^* (N/V_l)^2 r^{*3} \tag{13}$$

The value for c' depends on the form of the potential energy function as defined in eq. (11) or (12). The δ^2 value is a direct function of several equilibrium molecular properties. These, as we shall see, can be expressed in terms of individual molecular parameters. It is appropriate at this time to briefly describe the contributions to the total energy due to the various intermolecular interactions.

One should keep in mind that δ^2 is an all-inclusive term emphasizing the total strength of interactions in a liquid, not the individual energy contributions of each molecule. This situation can be remedied by assuming that the intermolecular interactions are due solely to dispersion, induction, and dipole forces.[26] The London equation for the dispersion interaction E_d gives the relationship between E_d, ionization potential I, and the molecular polarizability α. The ionization potentials of many organic liquids do not vary to any great extent. Normally, a value of 10 eV is given[27] for I, as in the case here:

$$E_d = 3\alpha^2 I/4r^6 \tag{14}$$

The dispersion forces are present in all molecules, polar and nonpolar. They allow strong, nondirectional attractions to exist between molecules. In molecules containing a dipole, an addition contribution to the energy dependent upon the dipole moment μ is found:

$$E_P = 2\mu^4/3kTr^6 \tag{15}$$

These forces are essentially electrostatic in nature. They differ from dispersion forces in that the direction of the dipoles with respect to one another affects the strength of this interaction. Polar forces are normally stronger than dispersion forces.

The interaction between a dipole and a nonpolar portion of a molecule sets up an induced charge in the latter, allowing an attractive interaction to take place. This interaction is weak but does have interaction characteristics similar to those observed in dipole forces. The energy contributed by the induction interaction is given by eq. (16):

$$E_i = 2\alpha\mu^2 r^6 \tag{16}$$

The induction effect may have a significant effect on δ^2 if the dipolar interaction is zero or close to zero.[16]

These three interactions are assumed to be additive; thus, it is possible to define the fractional contribution that each makes with respect to the total interaction energy. The fractional polarity p and the fractional contributions due to dispersion d and induction i forces are given in eqs. (17) to (20):

$$p = 2\mu^4/3kT\epsilon^* \tag{17}$$

$$i = 2\alpha\mu^2/\epsilon^* \tag{18}$$

$$d = 3I\alpha^2/4\epsilon^* \tag{19}$$

$$p + d + i = 1 \tag{20}$$

The above expressions for the fractional quantities involving intermolecular interactions can be modified to include an expression[24] which simplifies the final equations for

$$\epsilon r^{*6} = \frac{2\mu^4}{3kT} + \frac{3\alpha^2 I}{4} + 2\alpha\mu^2 \tag{21}$$

It should be noted the Gardon[27] has shown that d and i are both unique functions of p. Thus, when p is known, it is a relatively simple matter to obtain d and i.

Sufficient information has presently been derived concerning the description of the interactions between molecules to allow one to describe δ in terms of molecular parameters. Combining eqs. (14) and (18), one arrives at the result describing the dispersion contribution to δ:

$$\delta_d^2 = C'\pi \, (3I^2/4dr^{*3})(N^2/V_l^2) \tag{22}$$

Kaelble,[28] in a description of the liquid state, employed an equation connecting the liquid volume with the equilibrium intermolecular distance and the packing factor K:

$$V_l = Nr^{*3}/K \tag{23}$$

Finally, combining eqs. (22) and (23), we arrive at the final result using the LJP (c = 16/9):

$$\delta_d^2 = K(4\pi I\alpha^2/3d)(N/V_l)^3 \tag{24}$$

Utilizing the SP form of ϕ results only in a change in the value of the constant c'. Similarly, the polar and induction contribution to δ^2 can be obtained by combining eqs. (13) and (23) with eqs. (17) and (19), respectively:

$$\delta_p^2 = K(2\pi\mu^4/3kTp)(N/V_l)^3 \tag{25}$$

$$\delta_i^2 = K(2\pi\alpha\mu^2/i)(N/V_l)^3 \tag{26}$$

The derivation confirms that the total solubility parameter can be decomposed into three individual contributions based on three above-mentioned intermolecular interactions (hydrogen bonding excluded). It is well known[14] that a one-parameter δ is insufficient in predicting solubility of liquids, especially if one component possesses a significant dipole moment. This is so because of the noninterchangeable character of these intermolecular forces. Successful prediction of solubility is enhanced if the dispersion and polar components of δ^2 of both substances are similar. Thus, the adage "like dissolves like" can be interpreted in more specific terms when individual intermolecular interactions are included.

RESULTS AND DISCUSSION

The solubility parameter can be expressed as the sum of the contributions (due to the additivity of the intermolecular energies) of each of the individual intermolecular forces. As shown in the derivation, each contribution can be expressed as a function of both molecular and physical constants. These equations are not of sufficient accuracy for the prediction of δ^2. This situation is due to insufficient information in evaluating the constants in the above expression. The equations can be used, however, for interpretation (in terms of molecular quantities) of the various trends found in the use of δ^2 (or δ_d, δ_p^2, and δ_i^2).

It became necessary to use established values of the individual contributions to δ^2 for the evaluation of eqs. (26) and (27). Only these two contributions are considered here because permanent dipole-induced dipole forces are generally quite small as compared to the other forces.[29] In some cases this may not be totally accurate, as Meyer et al.[30] have found. For example, the higher molecular weight (fairly nonpolar) 2-ketones have approximately a 5–10% induction contribution to their cohesive energy density. Equations (26) and (27) will be further evaluated in terms of molecular volume. Included in this evaluation are any other factors not placed in the derivation, such as molecular packing differences between various liquids. This is in fact the major reason for using the experimental values for δ^2.

Initially, the discussion will focus on the dispersion contribution to δ^2. Rearranging eq. (24) and utilizing the definition of δ^2, eq. (13), the following expression for ΔE_d can be derived:

$$\Delta E_d = \frac{4}{3}\pi(I\alpha^2/d)N^3/V_l^2 \qquad (27)$$

The packing factor K is included in the term ΔE_d. The right-hand side of eq. (27) is evaluated as shown in Tables I and II. The appropriate sources for the molecular constants for each liquid are also included. The lists are quite extensive owing to the fact that many major groups of organic solvents do exist. Comparison of ΔE_d values with molecular size shows that both variables are proportional to each other. No further attempt was made to correlate any of these values with physical properties.

Figure 1 shows the correlation found between the ratio $\delta_d^2/\Delta E_d$ and the van der Waals volume v. A linear relationship exists between these two variables which, in turn, is approximately independent of the solvent group. Alkanes lie slightly above the line, while aromatics and ketones are below the line. This

TABLE I
Physical Quantities Pertaining to the Dispersion Contribution for δ of Selected Alkanes,
Aromatics, and Alcohols

Compound	V_l, cm³/mole[a]	d[a]	α, 10^{-23} cm³ [b]	eq. (29)	δ_d^2[c]	v, Å³ [d]
n-Pentane	116	1	1.03	241.3	49.7	96.4
Isopentane	117	1	1.02	255.1	49.7	96.4
n-Hexane	132	1	1.20	319.4	53.3	113.4
Cyclohexane	109	1	1.13	211.5	67.3	130.
n-Heptane	147	1	1.40	376.3	55.5	130.
n-Octane	164	1	1.59	462.5	57.0	147.
n-Nonane	180	1	1.75	568.8	58.5	164.
n-Decane	194	1	1.90	667.4	60.0	181.
Benzene	89	1	1.06	133.5	83.7	80.3
n-Propylbenzene	140	1	1.65	301.	74.8	131.6
Styrene	115	1	1.46	174.8	75.0	100.3
Methanol	41	0.547	0.33	22.6	55.1	36.1
Ethanol	57.5	0.672	0.50	50.	59.7	53.1
n-Propanol	76	0.800	0.71	91.2	60.1	70.1
n-Butanol	91	0.864	0.876	136.5	61.0	87.1
Cyclohexanol	104	0.888	1.13	166.4	72.3	109.7
n-Amyl alcohol	108	0.916	1.07	191.2	61.0	104.1
n-Hexanol	125	0.906	1.27	237.5	60.1	121.1
n-Heptanol	142	0.92	1.47	296.8	59.3	138.1
n-Octanol	158	0.94	1.63	395.	62.1	155.1

[a] Data obtained from Gordon[27]; d calculated using eq. (22) with p values from ref. 27.

[b] Polarizability calculated from the index of refraction (n) using the Lorentz–Lorenz equation; n values obtained from Handbook of Chemistry and Physics, 52nd ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1971–1972.

[c] Values of δ_d^2 taken from ref. 5.

[d] van der Waals volumes v calculated using Table 1 of J. T. Edward, J. Chem. Educ., 47, 261 (1970).

trend is most probably due to the differences in molecular shape and packing of the molecules. Trends observed[31] in the study of the physical properties of monomeric and polymeric substances reveal that the general overall shape of molecules has an influence on such properties as the melting and boiling points. The molar cohesion energy is found to be directly proportional to both the melting and boiling points in the lower molecular weight substances in a homologous series. Spherically shaped molecules possess higher phase transitions than either cylindrical, flat symmetrical, flat unsymmetrical, or asymmetric-shaped molecules. These latter four molecular symmetry descriptions are arranged in decreasing value of their phase transitions. It should be noted that parallel lines can be drawn through the points corresponding to each of these three groups mentioned above. The slope is found to be about the same in all cases, only the ordinate value changes slightly. The slope of the lines in Figure 1 is equal to 2, while the equation for the solid line is given[29] by

$$\log (\delta_d^2 / \Delta E_d) = 2 \log v + 1 \tag{28}$$

With the proper mathematical manipulations, eq. (28) can be converted into a more appropriate form:

$$(\delta_d / V)^2 = 10 \ \Delta E_d \tag{29}$$

The value of the constant (in this case 10) will change according to the units of

TABLE II
Physical Quantities Pertaining to the Dispersion Contribution for δ of Selected Ketones, Esters, Chlorine, and Nitrogen-Containing Compounds

Compound	V_l, cm³/mole	d	α, 10^{-23} cm³	eq. (29)	δ_d^2	v, Å³
Methyl ethyl ketone	89.5	0.424	0.824	68.9	60.4	81.8
Diethyl ketone	105.5	0.688	1.02	137.2	58.7	98.8
Cyclohexanone	109.	0.555	1.16	119.9	74.8	104.4
Methyl propyl ketone	106.	0.536	0.996	116.6	59.6	98.8
Methyl n-butyl ketone	122.	0.583	1.18	161.	60.1	115.8
Methyl hexyl ketone	156.	0.711	1.55	312.	61.6	149.8
Methyl formate	61.	0.632	0.508	54.9	56.4	54.
Ethyl formate	80.	0.822	0.825	81.6	57.5	71.
Methyl acetate	80.	0.765	0.825	75.2	57.2	71.
Ethyl acetate	99.	0.782	0.889	150.5	55.4	88.
n-Propyl acetate	115	0.824	1.06	213.9	58.	105.
n-Butyl acetate	132	0.782	1.25	257.4	58.8	122.
Aniline	91.	0.904	1.22	108.3	90.8	92.7
Pyridine	81.	0.774	0.946	915.	85.6	75.6
Acetonitrile	53.	0.106	0.44	76.9	62.4	47.1
Nitromethane	54.	0.170	0.495	109.1	64.5	50.8
Carbon tetrachloride	97.	1.	1.05	141.6	61.6	84.8
Chloroform	81.	0.965	0.863	124.1	74.8	70.7
1,2-Dichloroethane	79.	0.929	0.842	105.9	72.3	115.9
1,1-Dichloroethane	85.	0.729	0.856	100.3	67.1	115.9
Chlorobenzene	107.	0.91	1.31	168.	84.6	94.9
Bromobenzene	105.	0.946	1.35	154.4	85.6	99.6
1,2-Dibromobenzene	87.	0.973	1.08	89.6	65.6	83.

ᵃ The source of several of the values for the physical quantities given in this table are found in Table I.

molecular volume used. The explicit expression for ΔE_d is given in eq. (27). Thus, δ_d^2 can be expressed completely in terms of molecular parameters.

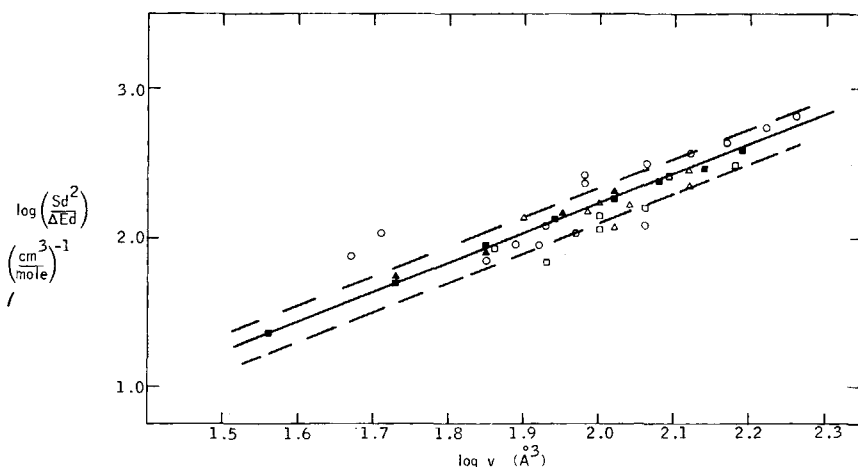Similar considerations, such as that given above, can be applied to the effect

Fig. 1. Correlation between ratio of the dispersion contribution of δ^2 to the energy of dispersion and the van der Waals volume. Symbol (O) refers to alkanes, while (■), (▲), (△), and (□) refers to aliphatic alcohols, acetates, aromatics, and ketones, respectively.

TABLE III
Physical Quantities Pertaining to the Polar Contribution for δ of Selected Solvents

Compound	V_l, cm³/mole[a]	p[a]	μ, debyes[b]	eq. (30)	δ_p^2 [b]	v, Å³ [c]
Methanol	41.	0.388	1.7	10.	36.	36.1
Ethanol	57.5	0.268	1.7	13.7	18.5	53.1
n-Propanol	76.	0.152	1.7	14.	10.9	70.1
n-Butanol	91.	0.092	1.7	13.	7.8	87.1
Cyclohexanol	104.	0.075	1.7	8.8	4.	109.7
Acetone	74.	0.695	2.9	16.2	26.	64.8
Ethyl acetate	99.	0.076* [a]	1.8	9.9	6.8	88.
n-Butyl acetate	132.	0.08*	1.9	12.7	3.2	122.
Methyl ethyl ketone	89.5	0.324*	2.7	16.1	19.4	81.8
Chlorobenzene	107.	0.058	1.6	10.8	4.4	94.9
Nitroethane	76.	0.710	3.6	17.	57.8	50.8
Aniline	91.	0.063	1.5	10.9	6.3	92.7
Pyridine	81.	0.174	2.2	12.6	18.5	75.6
Butyronitrile	87.	0.719	4.0	12.7	37.2	81.1
Nitrobenzene	103.	0.344*	4.3	8.6	36.	103.2
Chloroform	81.	0.017	1.2	17.	2.3	70.7
Methylene chloride	65.	0.12	1.5	8.6	9.6	56.6
Diethyl ether	105.	0.033	1.2	8.2	2.	85.6

[a] Data obtained from Gordon[27]; p values taken from ref. 15.

[b] Data obtained from Hansen.[15]

[c] van der Waals volumes v calculated using Table 1 of J. T. Edward, *J. Chem. Educ.*, **47**, 261 (1970).

of the polar contribution to δ^2. As shown in eq. (25), δ_p^2 is a function of the two molecular parameters μ and p. Rearranging eq. (25) and again using the definition of δ^2, eq. (13), the following expression for ΔE_p can be derived:

$$\Delta E_p = (2\pi\mu^4/3kTp)\, N^3/V_l^2 \tag{30}$$

Again the packing factor K is included in the term ΔE_p. Given in Table III are the values obtained in evaluating the right-hand side of eq. (30) from experimentally determined physical quantities. A broad range in the values of p and μ is found for the polar solvents used in this study.

Shown in Figure 2 is the plot obtained between the ratio $\delta_p^2/\Delta E_p$ and v. A correlation is observed that approximates a parabolic geometry (solid curve). In this case, however, the points will be connected by straight lines. The scatter
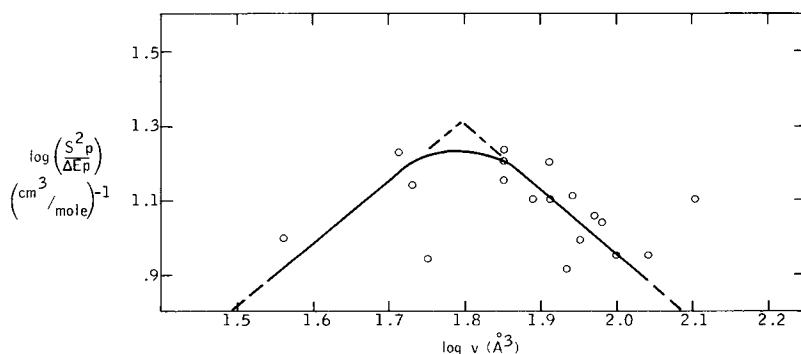

Fig. 2. Correlation between ratio of the dipole contribution of δ^2 to the dipole energy contribution and the van der Waals volume. Data are taken from Table III.

in the data is more prevalent than that observed in the study of the dispersion component to δ^2. The major reasons for this data scattering is due to both the molecular shape and the position of the dipole within the molecule. The calculation for the slopes of both lines gives the value of 2 for the line corresponding to points less than log 1.8. For points greater than 1.8, the slope is -2. It should be noted that the magnitude of slopes in both Figures 1 and 2 are equal to 2. The equations for the lines in Figure 2 are given below:

$$\log (\delta_p^2/\Delta E_p) = 2 \log v + 0.75 \qquad \log v < 1.8 \qquad (31a)$$

$$\log (\delta_p^2/\Delta E_p) = -2 \log v + 2 \qquad \log v > 1.8 \qquad (31b)$$

These two equations can also be converted into a more appropriate form:

$$(\delta_p/v)^2 = 10 \; \Delta E_p \qquad \log v < 1.8 \qquad (32a)$$

$$(\delta p/v^{-1}) = 10^2 \; \Delta E_p \qquad \log v > 1.8 \qquad (32b)$$

In eq. (32a) it is assumed that the exponent of 10 closely approximates 1. The explicit expression for ΔE_p is given in eq. (30). The important point to note is the similarity in form of the equations describing the molecular parameters that affect both the polar and dispersion contributions to δ^2. It can be assumed that because of this similarity in form, an expression describing δ_i^2 could be obtained by analogy.

The overall results indicate that δ_d^2 increases with molecular polarizibility and size, while δ_p^2 increases with dipole moment. δ_p^2 increases with molecular size up to about log v = 1.8; decreases are found with sizes larger than this. In all cases the molar volume is important as Robertson[32] confirmed in a study of cellulose–liquid interactions. Liquids having a molar volume greater than 100 cc did not increase the swelling of cellulose, even though some of these liquids were capable of strong hydrogen bonding with cellulose.

Equations (29) and (32) show that the molecular volume is also a factor to consider in using δ^2. The effects of molecular shape and size were observed in a study[33] of the solubility of various solvents in polymeric materials. The solubility of linear aliphatic hydrocarbons was found to decrease in polysulfone as the chain length of the hydrocarbon increased. This trend was found to hold true with lengths greater than pentane. In this study, solubility parameter considerations would have predicted increased solubility with chain length.

In the introduction it was noted that the cohesive energy density is used to establish relationships between itself and other physical phenomena, such as surface tension[34] and index of refraction.[35] In several cases[23,34,35] δ^2 is proportional to the physical quantity with a constant of proportionality C_1 that is not defined. For example, Keller et al.[35] related δ_d to the refractive index n:

$$\delta_d = C_1 \frac{(n^2 - 1)}{(n^2 + 2)} \qquad (33)$$

Systematic deviations from this equation do exist when $(n^2 - 1)/(n^2 + 2) > 0.3$. Combining eqs. (28) and (29) with the Lorentz–Lorenz function produces an equation relating δ_d with $(n^2 - 1)/(n^2 + 2)$, similar in form to eq. (34) but in this case the constant, C_1, is related to several parameters.

$$\delta_d = \frac{3}{2} v \left(\frac{IN}{d}\right)^{0.5} \left(\frac{n^2 - 1}{n^2 + 2}\right) \qquad (34a)$$

$$C_1 = \frac{3}{2} v \ (IN/d)^{0.5} \tag{34b}$$

(As predicted from the thermodynamic arguments presented here, C_1 is not constant but a function of molecular size.) Keller[35] noted that C_1 was truly constant only within a limited range of molecular sizes. Deviations from eq. (33) were not observed for relatively small molecules. Once the value for C_1 is established for small molecules, progressive deviations from this value is predicted to occur when the molecular size is increased. The experimental data confirm this trend.[35]

CONCLUSIONS

The solubility parameter concept has been used to describe a myriad of physical phenomena relating directly to the realm of intermolecular interactions. Miscibility of solvents with polymers, diffusion of solvents within polymers, effects of intermolecular forces on the glass transition temperature, interfacial interactions within copolymer materials, and solvent-induced crystallization would be included just to mention a few examples. In many cases meaningful interpretation of results was facilitated with the introduction of the solubility parameter. It includes all intermolecular interactions by definition, and there lies its inherent usefulness. Further refinements to this parameter could extend its applicability even further. Thus, as noted in this work, δ^2 can be described in terms of the components δ_d^2, δ_p^2, and δ_i^2. Each of these terms can in turn be described with known molecular parameters related principally to intermolecular forces and molecular size. For example, δ_d^2 is found to increase with molecular size, while δ_p^2 decreases with molecular size over most of the molecular size range studied. Initially, δ_p^2 increases in magnitude with relatively small molecular volumes. Finally, one observes that the mathematical form these expressions take are quite similar. The implications of the results found in this work in interpreting the effects of δ^2 on the physical properties of polymeric materials are presently being studied.

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