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AN EXPANDED SOLUBILITY PARAMETER TREATMENT FOR CLASSIFICATION AND USE OF CHROMATOGRAPHIC SOLVENTS AND ADSORBENTS

PARAMETERS FOR DISPERSION, DIPOLE AND HYDROGEN BONDING INTERACTIONS

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SUMMARY

A basis for calculating specific solubility parameters for dispersion, δ_d, induction, δ_{in}, orientation, δ_o, and hydrogen bonding, δ_a and δ_b, is presented. These parameters provide a classification scheme of solvents and adsorbents that can be used to estimate selectivity in chromatography. The dispersion solubility parameter is determined via the Lorentz–Lorenz function and the refractive index of the pure compound. The orientation parameter is obtained from the dipole moment of the substance and the molar volume. The use of bond dipoles (*i.e.* effective dipole moment) is found to be necessary in describing solution interactions. The induction solubility parameter can be obtained from the orientation parameter and the molar volume. For hydrogen bonding, the $\delta_a\,\delta_b$ product of alcohols obtained from the vaporization energy is correlated with the heat of hydrogen bonding. With the definition of equal values of δ_a and δ_b for alcohols, it is then possible to determine the parameters for other compounds via heats of hydrogen bonding. Evidence is presented of the general validity of the relationships derived.

INTRODUCTION

There is currently a need for a general classification scheme for solvents and adsorbents commonly used in chromatography. It is well known that ranking phase systems in terms of a single parameter, *e.g.* polarity, does not provide an adequate means of predicting retention and selectivity in chromatography. One must account for the various interaction forces that can occur between the solvent or adsorbent and the solute species. A general classification scheme ought to provide an understanding of the relationship between solute retention and the composition of chromatographic phase systems.

Practical schemes of retention to-date have been based on chromatographic data *per se*. For example, the group additivity approach (*e.g.* the Martin equation[1]), has been frequently employed[2–6]. Linear free energy approaches have also been taken[7–10]. More recently, factor analysis has been applied as a predictive tool for retention[11–14]. An approach for characterizing the polar aspects of solvents based on published data of gas–liquid partition[15] has been introduced[16].

Each of the above approaches for prediction and/or control of retention and selectivity can be quite useful in specific situations. However, a conceptually unified system for understanding and generalizing such schemes has so far been lacking. Ideally, such a treatment would be based on the fundamental intermolecular interactions common to both adsorption and partition systems —which have so far been treated separately. Finally, there should be a means to relate the various classification parameters to more readily available (*i.e.* non-chromatographic) data, such as the properties of pure compounds.

In a previous paper[17], we have outlined an expanded solubility parameter treatment for the general classification of solvents and adsorbents which is applicable to polar and nonpolar systems. This model is able to provide a means for estimating and understanding retention and selectivity in chromatography. Classification is based on a set of molecular characterizing parameters, the *specific solubility parameters*.

In the present paper, we will detail how specific solubility parameters can be derived from non-chromatographic data. A preliminary solubility parameter classification scheme of common solvents for liquid chromatography based on the approaches taken in this paper has already been published[18]. In a separate article[19] we outline in detail the applications and limitations of the method to the understanding of retention in the various forms of chromatography.

GENERAL MODEL

A general review of various expanded solubility parameter treatments has recently appeared[20]. In the original treatment of Hildebrand and Scott[21], the solubility parameter δ

$$\delta_i = \left(\frac{\Delta E_i^v}{V_i}\right)^{1/2} \tag{1}$$

(E^v = energy of vaporization per mole of pure i and V_i = molar volume), was assumed to be useful only for nonpolar systems. However, Blanks and Prausnitz[22] extended the treatment to polar (but non-hydrogen bonding) systems and Hansen[23] included both polar and hydrogen bonding interactions. As outlined in our previous paper[17], we have expanded on Hansen's approach.

To review briefly, ΔE_i^v represents the energy per mole required to overcome interactions between adjacent i molecules in the pure liquid state during the process of evaporation, if the gas phase is assumed to be ideal[21]. ΔE^v can in turn be subdivided into interaction energies per mole of the following type: dispersion $(E_{ii})^v_d$, induction

$(E_{ii})^{v}_{in}$, dipole orientation $(E_{ii})^{v}_{o}$, and hydrogen bonding $(E_{ii})^{v}_{hb}$, where subscript *ii* represents the interaction of adjacent *i* molecules. Each of these energy terms can be expressed as a product of specific solubility parameters[17]

$$V\delta^2 = (E_{ii})^{v}_{d} + (E_{ii})^{v}_{in} + (\Delta E_{ii})^{v}_{o} + (E_{ii})^{v}_{hb} = (\delta_d^2 + 2\delta_{in}\,\delta_d + \delta_o^2 + \\ + 2\delta_a\,\delta_b)\,V \qquad (2)$$

and δ_d^2 represents the contribution of dispersion interactions to ΔE^v, etc. Thus, δ_d indicates the ability of a substance to participate in dispersive interactions. Similarly, δ_o is a measure of the ability of a species to participate in dipole orientation interactions; δ_{in} the ability of that species to induce a dipole moment in surrounding molecules; and δ_a and δ_b the ability of that species to function as a proton donor or acceptor, respectively. For the present, we will not consider charge transfer interactions; however, if required, a term similar in form to that for $(\Delta E_{ii})^{v}_{hb}$ can be added to eqn. 1.

In the present paper we will consider methods by which the various solubility parameters can be calculated from properties of the pure compounds or mixtures. Eqn. 2 can be simplified to:

$$\delta^2 = \delta_d^2 + \delta_p^2 \qquad (3)$$

where δ_p is a composite quantity. Our approach will be to determine values of δ and δ_d from data on pure compounds. The dissection of resulting values of δ_p into inductive, orientation, and hydrogen bonding terms will then be performed in terms of certain theoretical considerations, as well as nonchromatographic data from mixed systems (solute plus solvent).

Values of δ can be determined from the energy of vaporization and the molar volume of a given compound (eqn. 1) at 25°. Hoy[24] has reported δ values for about 600 compounds, based on ΔE^v data.

In some cases ΔE^v values for the pure compounds are unknown, or the accuracy of such data is open to question. An alternative means for estimating ΔE^v is from the boiling point of the compound (Hildebrand rule)[25]

$$\Delta E^v = -3550 + 23.7\,T_b + 0.02\,T_b^2 \qquad (4)$$

where T_b is the absolute boiling temperature at 760 mm. Eqn. 4 has been verified previously[21] for a limited range of non-polar and slightly polar compounds. For *n*-alkanes and related alkyl derivatives above octane ΔE^v (and thus δ) values predicted by eqn. 4 are uniformly lower than experimental ΔE^v values[25]. Moreover, eqn. 4 is not useful for obtaining the δ values of species which significantly associate in the liquid state (*e.g.* water, alcohols)[25].

DISPERSION SOLUBILITY PARAMETER

Dispersive forces are common to the interaction of all molecules whether or not they possess a permanent dipole moment. For non-polar solutes, *e.g.* aliphatic and aromatic hydrocarbons, dispersion forces are the sole interacting forces in the pure liquid state with $\delta = \delta_d$, from eqn. 2. It should be noted that the δ values for acyclic hydrocarbons are found to be uniformly lower when calculated from the experimental ΔE^v, relative to the δ values obtained directly from solubility measurements (see eqn. 3 of ref. 17). Hildebrand and Scott[21] first noted this, and it has been further confirmed in the work of Rohrschneider[26] and Keller and Snyder[27]. (For example, in ref. 27 the solubility of anthraquinone in isooctane suggests that δ isooctane equals 8.1 rather than 7.3 (ΔE^v value)). Here we assume $\delta = \delta_d \approx 8$ for acyclic hydrocarbons above pentane as solvents. For the other hydrocarbon types (cyclic, aromatic), no discrepancy exists.

For polar compounds, the total solubility parameter is a sum of terms related to the various types of interaction (see eqn. 2). In order to examine the polar solubility parameter δ_p in detail (eqn. 3), it is necessary to have some means of estimating δ_d. Previous estimates of δ_d have been based on the homomorph principle[22,23] in which δ_d for a polar compound is taken to be equal to the δ value of a non-polar compound of roughly equivalent size and shape. This empirical approach is of limited accuracy. However, an accurate estimate of δ_d is necessary, since δ_p is determined from the difference of δ^2 and δ_d^2, and any errors in δ_d become magnified in δ_p.

In a previous paper[17] we have provided a different approach to estimating δ_d, based on the refractive index n of the compound in question. E_d (energy for dispersion interaction) is proportional to the square of the electron polarizability per unit volume, α_e^v. The Lorentz–Lorenz expression relates α_e^v and n (ref. 28),

$$\alpha_e^v = \left(\frac{3}{4\pi N}\right)\left(\frac{n^2 - 1}{n^2 + 2}\right) \tag{5}$$

where N is Avogadro's number. δ_d is then proportional to the refractive index function on the right hand side of this equation. A plot of δ for 96 hydrocarbons (with 8 or fewer alkyl carbon atoms) reveals a linear relationship[17]:

$$\delta_d = 30.7\left(\frac{n^2 - 1}{n^2 + 2}\right) \tag{6}$$

with a standard deviation in δ of ±0.2 units (*cf.* the homomorph approach in which the standard deviation in δ is ±0.7 units[23]). Most δ_d values are found to be less than 9.0 (see Table I); for δ_d values above this (including data for 13 additional non-polar non-hydrocarbons), the relationship with refractive index becomes non-linear

$$\delta_d = 2.24 + 53\,x - 58\,x^2 + 22\,x^3 \tag{7}$$

where x is the Lorentz–Lorenz refractive index function. The standard deviation for the hydrocarbons (polycyclic aromatics) remains at ±0.2 units while that for the non-hydrocarbons, *e.g.* CS_2, Br_2, is found to be ±0.4 units. The δ_d values in Table I have been calculated from eqn. 7.

We have previously[17] presented data in support of the use of eqns. 6 and 7 for the calculation of δ_d. As expected, when aliphatic groups are replaced by aromatic groups δ_d increases (*e.g.* for $C_6H_{13}COOCH_3$ $\delta_d = 7.6$, whereas for $C_6H_6COOCH_3$ $\delta_d = 9.1$). Also in a homologous series containing a single functional group, δ_p

decreases with increasing chain length. The change in δ_d per methylene group is small (*ca.* 0.2 units), leading to the useful approximations of $\delta \approx 8$ for aliphatic and $\delta \approx 9$ for aromatic hydrocarbons as solvents. Table I presents values of δ_d for a variety of solvents.

As seen in Table I and noted above, δ_d values do not vary greatly among simple organic compounds. Dispersion forces are thus non-selective, as is well known, and the significance, *per se*, of solvent δ_d values in chromatography is not great. For example, eluotropic strength in liquid chromatography is similar for all paraffin solvents[18]. The real significance of the δ_d values is to provide a basis for the calculation of δ_a values, which are concerned with selective interactions.

DIPOLE INDUCTION AND ORIENTATION SOLUBILITY PARAMETERS

Polar molecules, *i.e.* those possessing a permanent dipole moment (or bond dipole, see later) are capable of both dipole induction and orientation interactions in the pure liquid. For the present discussion we shall consider only compounds with a single polar substituent (the extension to multisubstituted compounds is discussed later), and we shall assume that no hydrogen bonding occurs in the pure liquid.

As previously[17], the net contribution of dipole induction in the pure liquid, $(E_{ii})^v{}_{in}$, can be written as

$$(E_{ii})^v{}_{in} = (2\delta_{in}\,\delta_d)^v \tag{8}$$

where

$$\delta_{in} = C_{in}\,\mu^2/V \tag{9}$$

and C_{in} is a constant for all compounds possessing a single polar substituent of dipole moment μ. Eqns. 8 and 9 arise from the fact that $(E_{ii})^v{}_{in}$ is proportional to the energy of a single induction interaction, $-2\mu^2\,\alpha_o/r^6$ times $1/V$ (proportional to concentration of dipoles in the pure liquid*), where α_o is the total polarizability of the molecule and r is the internuclear distance.

For dipole orientation we may write

$$(E_{ii})^v{}_o = \delta_o{}^2 V \tag{10}$$

It has been argued previously by us[17] and others[23,29,30] that the energy of a single dipole interaction is proportional to the product of the two dipole moments (μ^2 for the pure liquid), rather than the product of the squares of dipole moments predicted by the Keesom equation for two interacting dipoles in the gas phase. Combining these relationships with the product of the concentration of the two dipoles in the pure liquid ($1/V^2$) we have

$$\delta_o{}^2 = C_o{}^2\,\mu^2/V^2 \tag{11}$$

where C_o is a constant for compounds possessing a single polar substituent.

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[*] The assumption is made that there is a random distribution of dipoles throughout the pure liquid. If this were not so, then molecules with a single dipole moment would not follow Trouton's rule; however, as we have previously noted, only molecules which form hydrogen-bond complexes deviate significantly from this rule.

TABLE I

EXTENDED TABLE OF SOLUBILITY PARAMETERS

δ_T = Total solubility parameter from vaporization energy; δ_d = Dispersion solubility parameter; δ_o = Orientation solubility parameter; δ_{in} = Induction solubility parameter; δ_a = Proton-donor solubility parameter; δ_b = Proton-acceptor solubility parameter; V = Molar volume.

Solvent	δ_T *(cal/ml)*$^{1/2}$	$\delta_d{}^a$ *(cal/ml)*$^{1/2}$	δ_o *(cal/ml)*$^{1/2}$	δ_{in} *(cal/ml)*$^{1/2}$	δ_a *(cal/ml)*$^{1/2}$	δ_b *(cal/ml)*$^{1/2}$	V *(ml/mole)*
Perfluoroalkanes	*ca.* 6.0	*ca.* 6.0	—	—	1.0	—	—
n-Alkanes	*ca.* 8.0	*ca.* 8.0	—	—	—	—	—
Diisopropyl ether	7.1	6.9	1.0	0.1	—	3.0	102
Diethyl ether	7.5	6.7	2.4	0.5	—	3.0	105
Triethylamine	7.5	7.5	—	—	—	4.5	140
Cyclohexane	8.2	8.2	—	—	—	—	108
Propyl chloride	8.4	7.3	2.9	0.6	—	0.7	88
Carbon tetrachloride	8.6	8.6	—	—	—	0.5	97
Diethyl sulfide	8.6	8.2	1.7	0.25	—	2.6	108
Ethyl acetate	8.9	7.0	4.0	1.0	—	2.7	98
Propylamine	8.9	7.3	1.7	0.2	1.8	5.5	82
Ethyl bromide	8.9	7.8	3.1	0.6	—	0.8	77
Toluene	8.9	8.9	—	—	—	0.6	107
Tetrahydrofuran	9.1	7.6	3.5	0.8	—	3.7	82
Benzene	9.2	9.2	—	—	—	0.6	89
Chloroform	9.3	8.1	3.0	0.5	6.5	0.5	81
Ethyl methyl ketone	9.5	7.1	4.7	1.2	—	3.2	90
Acetone	9.6	6.8	5.1	1.5	—	3.0	74
1,2-Dichloroethane	9.7	8.2	4.2	0.5	—	0.7	79
Anisole	9.7	9.1	2.1	0.4	—	1.7	109
Chlorobenzene	9.7	9.2	1.9	0.3	—	1.0	102

Bromobenzene	9.9	9.6	1.5	0.2	—	1.0	105
Methyl iodide	9.9	9.3	2.5	0.3	—	0.7	62
Dioxane	10.1	7.8	5.2	1.0	—	4.6	86
Hexamethylphosphoramide	10.5	8.4	3.4	1.7	—	4.0	176
Pyridine	10.6	9.0	3.8	1.0	—	4.9	81
Acetophenone	10.6	9.6	2.7	0.7	—	3.3	117
Benzonitrile	10.7	9.2	3.4	1.0	—	2.3	103
Propionitrile	10.8	6.9	6.6	1.8	—	2.1	71
Quinoline	10.8	10.3	1.8	0.3	—	4.2	118
N,N-Dimethylacetamide	10.8	8.2	4.7	1.6	—	4.5	92
Nitroethane	11.0	7.3	6.0	2.2	—	1.0	71
Nitrobenzene	11.1	9.5	3.6	1.1	—	1.0	103
Tricresylphosphate	11.3	9.6	2.5	1.5	—	(?)	316
Dimethylformamide	11.8	7.9	6.2	2.4	—	4.6	77
Propanol	12.0	7.2	2.6	0.4	6.3	6.3	75
Dimethylsulfoxide	12.0	8.4	6.1	2.1	—	5.2	71
Acetonitrile	12.1	6.5	8.2	2.8	—	3.8	53
Phenol	12.1	9.5	2.3	0.4	9.3	2.3	92
Ethanol	12.7	6.8	3.4	0.5	6.9	6.9	59
Nitromethane	12.9	7.3	8.3	3.0	—	1.2	54
γ-Butyrolactone	12.9	8.0	7.2	3.2	—	(?)	77
Propylene carbonate	13.3	9.8	5.9	2.4	—	(?)	85
Diethylene glycol	14.3	8.2	4.0	0.6	5.3	5.3	96
Methanol	14.5	6.2	4.9	0.8	8.3	8.3	41
Ethylene glycol	17.0	8.0	6.8	1.1	6.1	6.1	56
Formamide	19.2	8.3	(?)	(?)	large	large	40
Water	23.4	6.3	(?)	(?)	large	large	18

* Calculated from eqn. 7.

If no hydrogen bonding occurs, then values of δ_p^2 (equal to $\delta^2 - \delta_d^2$) are given from eqn. 2 as

$$\delta_p^2 = \delta_o^2 + 2\delta_{in}\,\delta_d$$

$$\delta_p^2 = \delta_o^2\left(1 + \frac{2\delta_{in}\,\delta_d}{\delta_o^2}\right)$$

$$\delta_p^2 = \delta_o^2\,(1 + C\delta_d\,V) \tag{12}$$

where $C = (2C_{in}/C_o^2)$ is a common constant for compounds possessing a single polar substituent and for which no self association occurs in the pure liquid. Similarly, values of δ_{in} are given as

$$\delta_{in} = \frac{\delta_p^2 - \delta_o^2}{2\delta_d} \tag{13}$$

Eliminating δ_d between this relationship and eqn. 12 then yields

$$\delta_{in} = \frac{CV\delta_o^2}{2} \tag{14}$$

That there must be a relationship between δ_{in} and δ_o in these simple systems can be readily seen from eqns. 9 and 11.

Knowledge of C permits the calculations of δ_o and δ_{in} from the experimental values of δ_p, δ_d and V. C can in principle be evaluated from values of δ_p and δ_d for related compounds, but this is not an accurate procedure. A better approach is through the use of data for mixtures of a polar solute i and non-polar solvent j, in which induction interactions exists $(i + j)$, but orientation interactions are absent. These data can be conveniently obtained from gas–liquid chromatography (GLC)[31].

For GLC systems $\Delta E_{glc} = \Delta E^s$, the solution energy. From our previous work[17] and from a detailed paper to be published[19], it can readily be shown that for polar solutes and non-polar solvents

$$\Delta E_{glc} = V_i\,[(\delta_d^j)^2 - 2\delta_d^i\,\delta_d^j - 2\delta_{in}^i\,\delta_d^j] \tag{15}$$

Given experimental values of ΔE_{glc}, δ_d^i and δ_d^j, the value of δ_{in}^i can be calculated. This calculation is detailed in Appendix I for the GLC system in which *n*-hexadecane is the stationary phase. Next δ_o^2 (for the polar solute) can be calculated from $\delta_o^2 = \delta_p^2 - 2\delta_{in}\,\delta_d$. Finally, rearrangement of eqn. 14 gives

$$C = \frac{2\delta_{in}}{\delta_o^2\,V} \tag{16}$$

The derivation of values of C from data for widely different solutes in a particular GLC system (*n*-hexadecane solvent) is summarized in Table II. It will be noted that only solutes for which $\delta_p > 5$ have been selected. As δ_p becomes smaller, the derived C values show greater scatter, since δ_p is obtained by a subtraction of two squared quantities. The C values are seen to be approximately constant for all solutes

TABLE II

CALCULATION OF VALUES OF $C = 2C_{\text{in}}/C_o^2 = \dfrac{2\delta_{\text{in}}}{\delta_o^2 V}$ FROM GLC

Solute	*RI/100**	*V* *(ml)***	*δ**** *(cal/ml)*$^{\frac{1}{2}}$	δ_d *(cal/ml)*$^{\frac{1}{2}}$	δ_{in} *(cal/ml)*$^{\frac{1}{2}}$	δ_o *(cal/ml)*$^{\frac{1}{2}}$	*C* × *10*^{3} *(cal·ml)*$^{-\frac{1}{2}}$
$CH_3CH_2NO_2$	5.54	71	11.0	7.3	2.2	6.0	1.7
CH_3CH_2CN	4.85	71	10.8	6.9	1.8	6.6	1.2
$CH_3CH_2CH_2CN$	5.78	87	10.0	7.1	1.6	5.3	1.3
CH_3CH_2CHO	4.34	72	9.3	6.8	1.3	4.6	1.7
$CH_3COCH_2CH_3$	5.39	90	9.5	7.1	1.2	4.7	1.2
$CH_3CH_2CH_2CHO$	5.37	88	9.0	7.2	1.1	3.8	1.7
$CH_3COOCH_2CH_3$	5.46	98	8.9	7.0	1.0	4.0	1.3

* From ref. 31, recalculated data from ref. 41; liquid phase *n*-hexadecane.

** Data from ref. 42.

*** From vaporization energy[24].

and equal to $1.4 \pm 0.3 \times 10^{-3}$ (cal·ml)$^{-\frac{1}{2}}$. This will be taken to be a characteristic value for all monofunctional group organic solutes.

Given values of C, δ and δ_d, we can calculate values of δ_o and δ_{in} for those solutes in which hydrogen bonding does not occur in the pure liquid state. Some of these values are reported in Table I. With these derived δ_o and δ_{in} values, we are now in a position to check some of the basic tenets of the model, for the case in which no hydrogen bonding occurs.

The validity of the δ_{in} values (and hence the value of C) can be in part examined by comparing $(E_{ii})_{\text{in}}$ calculated from eqn. 8 with experimentally estimated $(E_{ii})_{\text{in}}$ values[32]. This is done in Table III in which $(E_{ii})_{\text{in}}$ is taken as the interaction energy of induction between the given solute and Apiezon M, as estimated by gas chromatography. A value of 8 is taken for δ_d for the stationary phase. Considering the approximations, the agreement between the two values of $(E_{ii})_{\text{in}}$ is satisfactory.

Further examination of the model can proceed in the following manner. Eqn. 11 states that the interaction energy E_o for dipole orientation is proportional to μ^2, rather than μ^4 as given by the Keesom equation. However, it must be remembered that the μ^4 dependence is calculated for the gas phase in which rotation allows the interacting dipoles to assume a variety of positions in relation to one another. In solution, the roughly thousandfold increase in density (relative to the gas phase) makes intermolecular distances shorter, thus restricting rotation. Hansen in his expanded

TABLE III

COMPARISON OF $(E_{ii})_{\text{in}}$ VALUES FOR SOLUTION OF SOLUTE IN APIEZON M CALCULATED FROM eqn. 8 WITH PUBLISHED VALUES

δ_d for Apiezon M assumed to be equal to 8.

Solute	V_t	δ_{in}	$(E_{ii})_{\text{in}} = 2\delta_{\text{in}}\delta_d V$	$(E_{ii})_{\text{in}}$*
Chloropentane	121	0.4	0.8	0.8–1.1
Acetone	73.5	1.2	1.1	1.3
Capronitrile	121	1.1	2.1	2.0–2.1

* Data from ref. 32.

solubility parameter model employed a μ^2 dependence[25]. In addition, Bondi[29] has suggested the μ^2 dependence for crystals and Weiner *et al.*[30] using factor analysis in GLC find this relationship. We shall now examine further the relationship of δ_o to μ.

The calculation of δ_{in} and δ_o in Appendix I makes no assumption concerning the dipole moment dependence of either of these solubility parameters. From the constancy of C in Table II, it follows from eqn. 16 that δ_o^2 and δ_{in} must have the same functional dependence on the dipole moment. If eqn. 9 is assumed to be correct, then it must follow that eqn. 11 is also correct or $\delta_o^2 \propto \mu^2$.

Further proof that $\delta_o^2 \propto \mu^2$ can be seen as follows. The polar solubility parameter, δ_p, can be calculated from eqn. 3. If no hydrogen bonding occurs, we have from eqns. 9 and 11

$$\delta_p^2 = \frac{C_o^2 \mu^2}{V^2} + \frac{2C_{in} \mu^2}{V} \delta_d \tag{17}$$

or with $\delta_d = 8$

$$\delta_p^2 = \frac{C_o^2 \mu^2}{V^2} [1 + 12.8 \times 10^{-3} V] \tag{18}$$

For a homologous series of a given functional group, eqn. 18 can be written as

$$\delta_p^2 = C_o^2 \mu^2 \mathrm{f}(V) \tag{19}$$

where μ is approximately constant. Fig. 1 shows plots of log δ_p *vs.* log V for different homologous series, and it is found that parallel straight lines give a good approximation of the data, *i.e.* the common function $\mathrm{f}(V) \approx V^{-0.7}$. This functionality follows directly from the separate volume dependencies of the induction and orientation terms of $V^{-\frac{1}{2}}$ (eqn. 9) and V^{-1} (eqn. 11). Included in Fig. 1 is the log δ_p *vs.* log V plot for *n*-alcohols. The self-association possible in this case leads to $\mathrm{f}(V)$ functionality of $V^{-0.5}$. Thus, the reduction in δ_p with molar volume occurs more slowly when hydrogen bonding results. We will discuss in detail hydrogen bonding in the next section.

As we have already noted, δ_d does not change significantly from compound to compound in a homologous series. If $\delta_d \approx 8$ for aliphatics, then from eqns. 12 and 18 it can be seen that when $V = 78$ ml, the contributions of induction and orientation to δ_p are equal, *i.e.* $\delta_o^2 = 2\,\delta_{in}\,\delta_d$.

From the results of Fig. 1, monofunctional group systems (without hydrogen bonding) can be placed on a common basis for comparison in terms of the value of δ_p at a constant molar volume. We have arbitrarily selected $V = 78$ ml for this purpose, as the induction and orientation terms are equal at this point.

From eqn. 17 and our discussion of the dipole moment relationship to E_o, $(\delta_p)_{V=78\text{ ml}}$ should be directly proportional to μ. This relationship is tested in Fig. 2, and it can be seen that a straight line exists for most monofunctional compounds. The ester, RCO_2CH_3, is more polar than predicted from the dipole moment. This results from the fact that the overall dipole moment of the ester is the sum of two dipole vectors which are partially in opposite directions, causing some cancellation. Yet in solution, as we have pointed out, single (bond) dipoles from two molecules interact at close range with each other, and therefore it is the individual bond dipoles

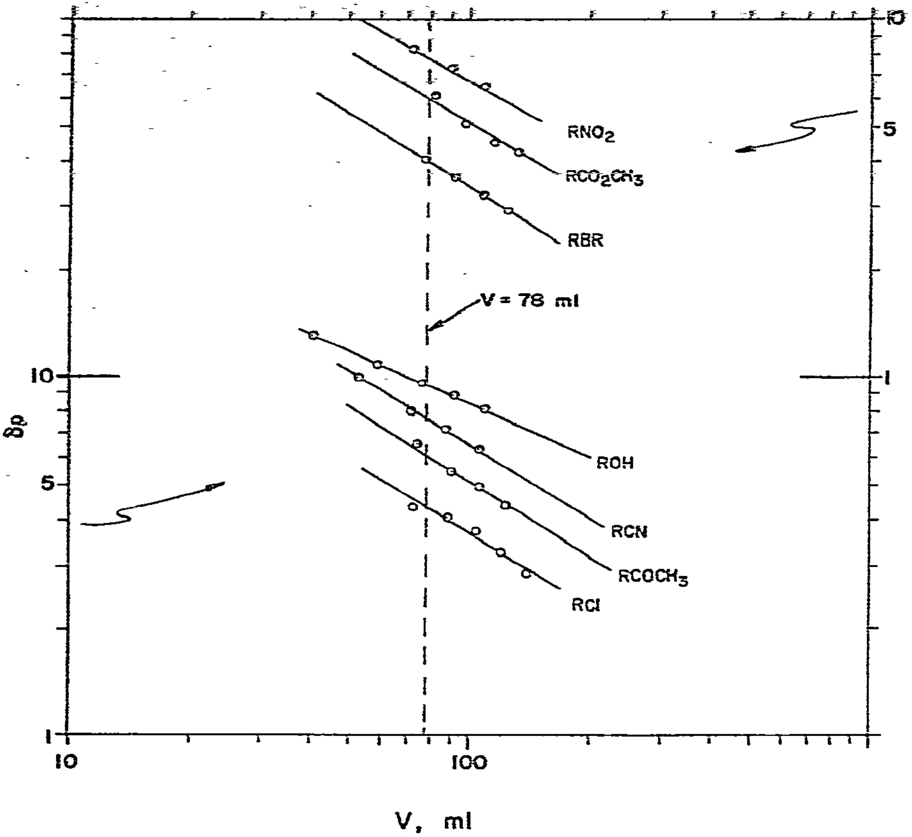

Fig. 1. Plot of log δ_p *vs.* log V (molar volume) for homologous series of monofunctional group compounds.

that interact. $(\delta_p)_{V=78\text{ ml}}$ for ester is close to that of ketone $RCOCH_3$, which suggests that it is the carbonyl on the ester linkage which mainly partakes in dipole orientation. Fig. 2 can then be used to define an "effective" dipole moment for esters in solution (and the adsorbed state)[28]. Further, other functional groups (that do not self associate) deviating from the straight line can have their dipole moments redefined to reflect the actual polarity of the group.

The final example of the μ^2 dependence of E_o can be obtained from gas chromatographic data. If no hydrogen bonding takes place, it is easy to show that[19]

$$\Delta RI = -\frac{100\,V_i}{\Delta E^j_{me}}(2\delta_o^i\,\delta_o^j) \tag{20}$$

where ΔRI is the retention index difference of a solute between a polar and nonpolar stationary phase and ΔE^j_{me} is the methylene group increment contribution to ΔE_{glc} in solvent j. If a common polar solvent is used, then ΔRI should be proportional to μ_i for a series of monofunctional group compounds from eqn. 11.

Fig. 3 is a plot of ΔRI *versus* μ_i for such a series of compounds, the polar phase being *n*-hexadecylnitrile and the non-polar phase being n-hexadecane[31]. It can be seen

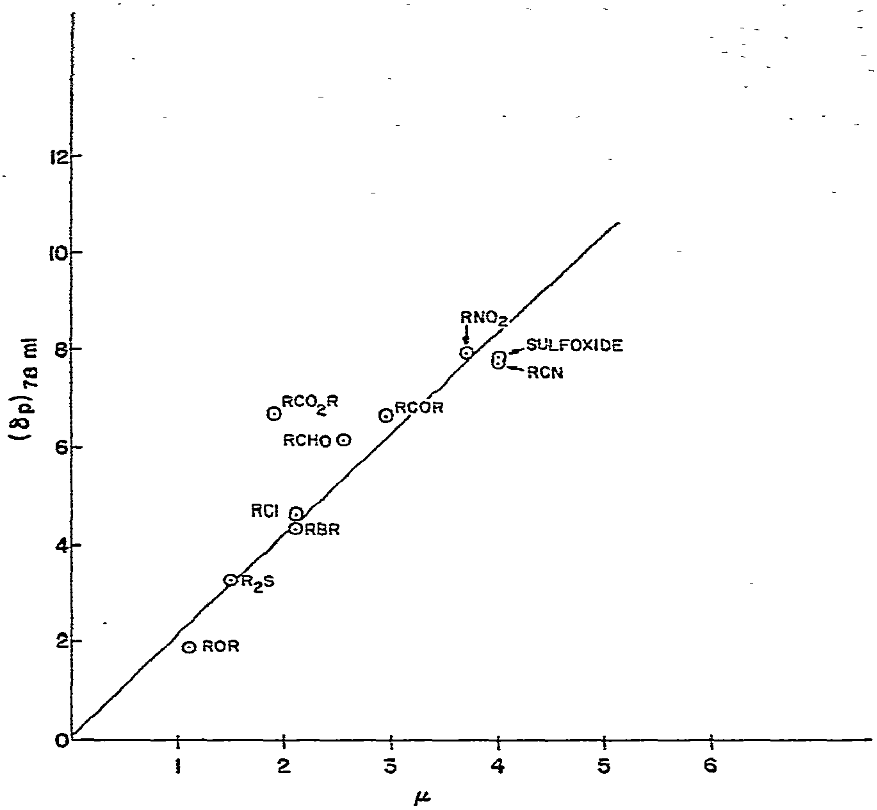

Fig. 2. Plot of $(\delta_p)_{V\,=\,78\,\mathrm{ml}}$ *vs.* gas-phase dipole moment for monofunctional group compounds.

that a linear relationship exists with a zero intercept. (Kováts has already noted the same relationship[31]). As previously, methyl acetate falls off the line, a result of the use of the gas phase dipole moment for dipole orientation interactions, rather than the effective dipole moment.

So far we have dealt solely with monofunctional group systems. As more functional groups are placed in the molecule and as the molecule becomes more complex, the relationships must be modified. Let us examine several of these cases.

Consider first a molecule with two equivalent functional groups well removed from one another such that there is no intramolecular interaction, *e.g.* $Cl{-}(CH_2)_4{-}Cl$. Although the total dipole moment is near zero, the concentration of local dipoles will be twice as large as that of a single functional group, or $2/V$. If the dipole moment (effective where necessary) of the single substituent is used (in this case R–Cl), then eqns. 9 and 11 become

$$\delta_{in} = \frac{2C_{in}\mu^2}{V} \tag{21}$$

and

$$\delta_o^2 = \frac{4C_0^2\mu^2}{V^2} \tag{22}$$

The molar volume at which $\delta_o^2 = 2\delta_{in}\,\delta_d$ is consequently reduced by a factor of 2, to 39 ml.

If the two functional groups on the molecule are different, then to account for all possible dipole orientations and inductions we have

$$\delta_{in} = \frac{C_{in}}{V}\,[\mu_1^2 + \mu_2^2] \tag{23}$$

and

$$\delta_o^2 = \frac{C_0^2}{V^2}\,[\mu_1 + \mu_2]^2 \tag{24}$$

where μ_1 and μ_2 are the dipole moments for the two functional groups. Note that when $\mu_1 = \mu_2$, eqns. 23 and 24 reduce to 21 and 22, respectively. We can generalize the expressions for n different functional groups that are independent of one another as

$$\delta_{in} = \frac{C_{in}}{V}\sum_i^n \mu_i^2 \tag{25}$$

and

$$\delta_o^2 = \frac{C_0^2}{V^2}\left(\sum_i^n \mu_i\right)^2 \tag{26}$$

The characterization of molecules in which intramolecular effects influence intermolecular interactions is more complex. In general steric effects will prevent the close approach of molecules (or dipoles) to the functional group, thus effectively decreasing δ_o, δ_{in}, and hence δ_p. Electronic effects can either enhance or diminish polar interactions, depending on their relative influence on the dipole moment of the polar functional group. While some simple rules might be applied to estimate these effects (*e.g.* refs. 33 and 9), these rules are restricted to specific cases. It seems best for the present to calculate δ_p from vapor pressure measurements and to ascertain the effective dipole moment in a fashion similar to that used in Fig. 2. Turning the problem around, measurement of the effective moment for specific molecules can provide useful information in understanding the first-order influence of steric and electronic effects on intermolecular forces.

HYDROGEN BONDING SOLUBILITY PARAMETERS

As discussed later by us and noted by others[20], extension of the solubility parameter approach to hydrogen bonding is more approximate than extention to dipole interactions. Nevertheless, correlations of the δ_a and δ_b with heats of hydrogen bonding can provide useful characterization for hydrogen bonding.

The approach begins with a consideration of *n*-alcohols, for which self association in the pure liquid state exists. In this case all the terms in eqn. 2 are necessary in order to account for all interactions in the bulk liquid phase. Consider ethanol for which $\delta = 12.7$, as calculated from vapor pressure data[24]. The value of the dispersion solubility parameter δ_d is then obtained from eqn. 6 and the refractive index, and is found to be 6.8 (see Table I).

In order to determine the value of $2\delta_a\,\delta_b$ for ethanol, we must next calculate the terms for dipole orientation and induction in eqn. 2. This can most readily be accomplished by assuming that the linear relationship between $(\delta_p)_{V=78\,\mathrm{ml}}$ and dipole moment μ is valid for the polar solubility parameter of ethanol without hydrogen bonding, δ'_p. Since the dipole moment is 1.70, $(\delta'_p)_{V=78\,\mathrm{ml}} = 3.2$, from Fig. 2. This value can be corrected to the molar volume of ethanol which is 58.5 ml/mole, by recalling from Fig. 1 that for non-hydrogen bonding monofunctional group classes $\delta_p = AV^{-0.7}$. Thus δ'_p for ethanol is 4.5, excluding hydrogen bonding. The values of δ_0 and δ_{in} can be obtained from this value and eqn. 14. The small dipole moment found for the alcohols minimizes errors from this approach.

We next arbitrarily assign $\delta_a = \delta_b$ for all n-alcohols. A definition on the relationship of δ_a to δ_b is necessary, since absolute values for proton donating and accepting abilities of molecules cannot be obtained (*cf.* single ion activities in salt solutions). In effect δ_a and δ_b values for all solutes are made relative to the values for n-alcohols. This particular definition has no practical consequence, since in all hydrogen bonding interactions the product $\delta_a\,\delta_b$ is the term that accounts for the interaction.

From the values of δ, δ_d and δ'_p for ethanol, we calculate that $\delta_a = \delta_b = 6.9$. Following similar calculations for other n-alcohols, we find the δ_a and δ_b values for alcohols shown in Table I. It is easy to ascertain that $\delta_a = \delta_b \propto V^{-\frac{1}{2}}$ from the results in the table. This molar volume dependence has already been seen in the plot of log δ_p *vs.* log V for the n-alcohols in Fig. 1. The consequence of this dependence is that dipole forces reduce more rapidly with molar volume than hydrogen bonding forces.

The calculation of δ_a and δ_b for non-self-associating species requires the heats of hydrogen bond formation determined by procedures such as infrared spectroscopy[34], NMR[35] and calorimetry[36]. We have selected the ΔH values measured by Arnett *et al.*[37] and Drago *et al.*[38] for this paper.

Our first task is to relate the values of $\delta_a\,\delta_b$ determined for the n-alcohols to the heat of hydrogen bonding. For a given n-alcohol:

$$\Delta H_{hb} = C^* V\delta_a\,\delta_b \tag{27}$$

where C^* is a proportionality constant common for all n-alcohols. The value of ΔH_{hb} for n-alcohols is taken as -5200 cal/mole[39]. For n-alcohols from methanol to n-hexanol, we find a value of C^* equal to 1.8 ± 0.05.

Consider next the hydrogen bond interaction of n-butanol with a series of bases, ΔH_{hb} values of which have been published[37]. We may alter eqn. 27 to

$$\Delta H_{hb,i,j} = 1.8\,[V_i^{\frac{1}{2}}\,\delta^i{}_a]\,[V_j^{\frac{1}{2}}\,\delta^j{}_b] \tag{28}$$

The assumption is made that the value of C^* remains the same as that obtained for the n-alcohols. The consequences of this assumption are discussed shortly. From the ΔH_{hb} values for a series of bases interacting with n-butanol, δ_b values are obtained, as shown in Table I. The δ_a values for acids can then correspondingly be calculated from ΔH_{hb} values with given bases and are again shown in Table I.

For a difunctional base such as dioxane, the concentration of base groupings is twice as great as for monofunctional bases. The δ_b value calculated from ΔH_{hb} must therefore be multiplied by $\sqrt{2}$; hence the δ_b value of 4.6 for dioxane as seen in

Table I. For substances such as phenol which self-associate in the pure liquid state, the opposite hydrogen-bonding parameter can be calculated from the energy of vaporization and eqn. 2.

A cursory examination of the values of δ_a and δ_b in Table I reveals that the order of substances in terms of "proton donating" and "proton accepting" ability is qualitatively correct. Thus, proton acceptors such as pyridine and dimethylsulfoxide are found to have higher δ_b values than weaker acceptors such as diethyl ether and methyl ethyl ketone. A closer examination is shown in Table IV where δ_b values for common basic solvents are listed. As already noted, the δ_b values are dependent on molar volume. Multiplication of δ_b by the square root of the molar volume makes the proton accepting parameter proportional to the heat of hydrogen bonding, which to a first approximation should not depend on the size of the molecule (steric and electronic effects are assumed negligible). Some changes in the order of the solvents is observed with this correction. Thus, tertiary amine is found to be a stronger acceptor than sulfoxide while the δ_b value of triethylamine is smaller than that of dimethylsulfoxide. It should also be emphasized that hydrogen bonding is only one of several polar interactions. Thus, while acetonitrile appears to accept protons less readily than pyridine (Table IV), the former solvent may often be more "polar" as a result of its large δ_o value.

TABLE IV

PROTON ACCEPTOR ABILITIES OF VARIOUS SOLVENTS

Solvent	*V* *(ml/mole)*	δ_b *(cal$^{\frac{1}{2}}$·ml$^{-\frac{1}{2}}$)*	$V^{\frac{1}{2}}\delta_b$ *((cal/mole)$^{\frac{1}{2}}$·10)*
Alkanes	—	0	0
Benzene	89	0.5	4.7
n-Butyl chloride	104	1.0	10
Anisole	109	1.7	17
Diethyl sulfide	108	2.6	27
Ethyl acetate	98	2.7	27
Diethyl ether	105	3.0	31
Ethyl methyl ketone	90	3.2	30
Acetonitrile	53	3.8	28
Quinoline	118	4.2	46
N,N-Dimethylacetamide	92	4.5	43
Triethylamine	140	4.5	54
Pyridine	81	4.9	47
Dimethylsulfoxide	71	5.2	45
n-Propylamine	82	5.5	50
n-Propanol	75	6.3	55

The values of δ_a and δ_b must be considered approximate for several reasons. First, the model has neglected the entropy change involved in the formation (or dissociation) of a hydrogen bond. A partial correction for entropy is incorporated into the empirical constant C^*, as a linear relationship exists between ΔH_{hb} and ΔS_{hb}[40]. However, the use of the same value for C^* for all hydrogen bonding interactions assumes that a common equation of ΔH_{hb} and ΔS_{hb} exists for all proton donating and proton accepting pairs, which is clearly not correct. As we do not know the propor-

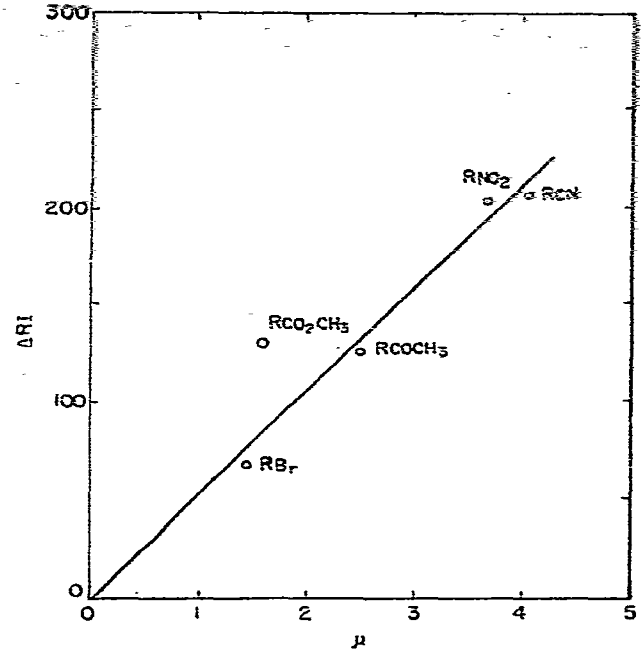

Fig. 3. Plot of ΔRI (*n*-hexadecylnitrile–*n*-hexadecane) *vs.* gas-phase dipole moment for monofunctional group compounds.

tionality constant of ΔH_{hb} and ΔS_{hb} for all cases, the only reasonable approximation is to assume C^* is constant throughout.

Second, the assumption is made that dipole and induction forces remain the same whether or not hydrogen bonding occurs. While this assumption is open to argument, it needs to be noted that the practical significance is not great as generally either hydrogen bonding or dipole interactions predominate when two polar molecules interact. Nevertheless, in spite of the approximate nature of δ_a and δ_b, it is still possible to employ these parameters for classification of solvents and adsorbents[19].

CONCLUSIONS

This paper has detailed how the component parts of the solubility parameter can be calculated from various non-chromatographic data. Most emphasis has been placed on solvents; however, in a separate paper[19] the calculation of polar specific solubility parameters for adsorbents is detailed. That paper[19] also explores the relative accuracy of the solubility parameter approach, and its utility in guiding the selection of specific chromatographic phases for given applications. The approach will also be shown to provide a rational unification of chromatographic processes.

Since the completion of this manuscript, a paper on an expanded solubility parameter approach for estimation of chromatographic retention has appeared[43]. While that paper follows along lines similar to the approach taken in the present work, there are some important differences which will be elaborated upon elsewhere[19].

ACKNOWLEDGEMENT

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APPENDIX I

Calculation of $C = 2C_{in}/C_o^2 = \frac{2\,\delta_{in}}{\delta_o^2\,V}$

Gas–liquid chromatographic data can be conveniently used to calculate δ^i_{in} and hence the relative contributions of dipole orientation and induction to the solubility parameter. Consider the retention of *n*-alkane solutes (i) on *n*-hexadecane (j). Since only dispersion forces are present in this system ΔE_{glc} can be written as[19]

$$\Delta E_{glc} = V_i\,[(\delta^j_d)^2 - 2\delta^i_d\,\delta^j_d] \tag{A-1}$$

The ΔE_{glc} can be calculated from the δ_d values of the *n*-alkanes and δ^j_d for *n*-hexadecane ($\delta_d = 8$). A plot of ΔE_{glc} *vs.* carbon number n results in a straight line. A least-squares analysis of this line between $n = 4$ and $n = 8$ results in the generalized expression

$$\Delta E_{glc} = -1240\,n + 500 \tag{A-2}$$

ΔE_{glc} values for polar solutes of retention index RI can now be calculated from eqn. A-2, substituting RI/100 for n. The RI values at 22–23° for polar solutes are obtained from Kováts and Weiss[31]. Eqns. A-2 and 6 can then be combined to give

$$\delta^i_{in} = \frac{1240\,\frac{\mathrm{RI}}{100} - 500 + V_i\,(64 - 16\,\delta^i_d)}{16V_i} \tag{A-3}$$

where $\delta_d = 8$ for *n*-hexadecane. The δ_{in} values of Table II are calculated from this equation.

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