FUNDAMENTAL, PREDICTIVE APPROACH TO DIPOLE–DIPOLE INTER-ACTIONS BASED ON THE DIPOLE MOMENT OF THE SOLUTE AND THE DIELECTRIC CONSTANT OF THE SOLVENT

PETER W. CARR

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455 (U.S.A.)
(First received October 22nd, 1979; revised manuscript received January 31st, 1980)

SUMMARY

A new solvent polarity scale, the Taft π^* scale, is explored for its utility in predicting partition coefficients and solubility parameters of non-hydrogen-bonding, non-aromatic solvents. A function of the dielectric constant of the solvent and the dipole moment and molar volume of the solute is used to obtain *a priori* estimates of orientation (permanent dipole–permanent dipole) solubility parameters. The correlation coefficient between measured and predicted orientation solubility parameters is 0.97; the slope is close to unity.

INTRODUCTION

Although great progress has been made in understanding the many factors which influence the efficiency of chromatographic systems[1], one of the chief remaining problems in separation science is the primitive level of understanding of the intermolecular processes which are the driving force for the separation. A complete theoretical understanding of intermolecular interactions would permit the *a priori* estimation of the equilibrium constant (defined below) for the transfer of solute from the mobile to the stationary phase:

$$A_{(mobile)} \rightleftharpoons A_{(stationary)} \tag{1}$$

$$K_{eq} = \frac{[A]_s}{[A]_m} \tag{2}$$

If such partition coefficients (K_{eq}) could be predicted, then one could rationally choose the most appropriate mobile and stationary phases for a particular separation.

There are many approaches to the prediction of solute retention. Most methods rely upon a combination of theory and experiment. These approaches include: factor analysis, which attempts to identify chromatographically significant molecular parameters[2] (*e.g.* refractive index and dipole moment); Snyder's empirical

solvent strength scale (ε^0) for adsorption chromatography[3]; the use of functional group parameters[4] and linear free energy relationships[5]; and the Rohrschneider–McReynolds multiple test solute retention scheme[6,7], which has been used as the basis for both gas chromatographic (GC) and liquid chromatographic (LC) solvent polarity scales, and selectivity classifications[8–10].

One of the most important and fundamental approaches to quantifying intermolecular interactions is the solubility parameter concept developed by Hildebrand *et al.*[11]. Chromatographic applications of this concept have been widespread[12,13]. In its original form, the solubility parameter was thought to be strictly applicable only to interactions which obey a geometric mean relationship, *e.g.*, London dispersion interactions. The approach has been used, even by Hildebrand *et al.*[11], to estimate the strength of polar interactions which may not follow a geometric mean interaction. In recent work, the solubility parameter has been treated as a multi-dimensional quantity which represents the totality of dispersion (δ_d), orientation (δ_o), induction (δ_{in}), and hydrogen-bonding donor (δ_a) and acceptor (δ_b) contributions. In accord with common usage, orientation processes, represented by δ_o, refer to the interaction between two permanent dipoles. Induction processes (δ_{in}) refer to the interaction which occurs when a permanent dipole induces a dipole in a normally non-polar but polarizable molecule. As will develop, our main interest here is in the interaction of two permanent bond dipoles. Keller *et al.*[14] and Karger *et al.*[15] have presented a systematic approach to evaluating all of these individual solubility parameters and have done so for a series of common solvents. They have also derived relationships between individual solubility parameters and important chromatographic measures of retention, such as partition coefficients for gas–liquid, liquid–liquid, and adsorption chromatography, and they have related solubility parameters to Kováts' retention index, adsorbent solvent polarity, and functional group adsorption energies[16].

From a chromatographic viewpoint, intermolecular interactions fall into three broad classes: dispersion interactions, which are general and relatively non-selective; simple polar interactions, *i.e.* those due to permanent dipole and induced dipole moments, which are somewhat selective; and a number of very selective interactions which may be described as various hard–soft acid–base processes such as hydrogen bonding. Of these various forces, only dispersion interactions have been successfully predicted from fundamental molecular properties. Keller *et al.*[14] and Karger *et al.*[15] were able to correlate the solubility parameters (within ± 0.2 (cal/ml)$^{1/2}$) of nearly 100 hydrocarbons with a simple function of the refractive indices of these compounds. They used this correlation to dissect the total solubility parameter of polar compounds into dispersion and net polar contributions. The homomorph approach[11] to the estimation of the dispersion contribution to the total solubility parameter is useful to within ± 0.7 (cal/ml)$^{1/2}$ for the same set of compounds[15].

In addition to the polarity indices mentioned above, physical chemists have described a variety of solvent polarity scales which have been rather neglected by chromatographers. These scales (see Table I) include: Dimroth's[17] E_T, Brooker's[18] χ_R, Lassau and Jungers'[19] log k (Pr_3N + MeI), Walther's[20] E_K, Knauer and Napier's[21] A_N, Allerhand and Schleyer's[22] G, Taft's[23] P, and Braunstein's[24] S. These scales are based on the dependence of some characteristic of either a test molecule or reaction on the nature of the solvent. Generally, this includes the effect of solvent on a reaction rate or equilibrium constant, or the effect of solvent on some spectroscopic property, such

TABLE I

TAFT CORRELATION OF EMPIRICAL SOLVENT POLARITY SCALES[1]

n = Number of solvents included in the linear regression; ϱ = linear regression correlation coefficient.

Scales correlated[11]	n	ϱ
μ vs. π^*	23	0.985
E_T vs. π^*	12	0.987
χ_R vs. π^*	16	0.987
$\log k$ vs. π^*	13	0.985
E_K vs. π^*	9	0.977
A_N vs. π^*	6	0.993
G vs. π^*	8	0.993
P vs. π^*	12	0.989
S vs. π^*	10	0.981

[1] Data from ref. 26. The solvents employed are listed therein.
[11] See text for references to the scales employed.

as the nuclear magnetic resonance, infrared or ultraviolet absorption energy of a solvent-sensitive transition.

The most recent and perhaps the most extensive such scale is the Taft system, which is based on the effect of solvent on the frequency of maximum absorption of the $\pi \to \pi^*$ or p $\to \pi^*$ transition of a judiciously chosen set of test solutes[25-27]. In the absence of specific interactions such as hydrogen bonding, Taft and coworkers have shown that certain properties (denoted $(XYZ)_o$), which are linear with respect to free energy, are related to their solvent scale as follows:

$$(XYZ)_o = (XYZ)_c + s(\pi^* + d\triangle) \qquad (3)$$

$(XYZ)_c$ denotes the value of the measured variable in cyclohexane, which is taken as the reference solvent in their system ($\pi^* = 0$). π^* is the solvent polarity parameter, s is the susceptibility of the variable $(XYZ)_0$ towards solvent polarity changes. The term $d\triangle$ accounts for the enhanced polarizability and other effects involved in aromatic and halogenated solvents.

They have observed that for a class of solvents, which is termed "select", namely aprotic, aliphatic solvents with a dominant bond dipole, all of the empirical solvent polarity scales listed in Table I give equivalent results[26]. This is a very significant finding since the parameters correlated encompass a wide range of observables. Obviously, there must be a single physical process characteristic of the effect of the solvent on all of these variables. In a subsequent paper, Abboud and Taft[27] showed an excellent linear correlation between the empirical π^* values and a simple function of solvent dielectric constant (D). The relationship between π^* and D was obtained from Block and Walker's[28] modification of Kirkwood's equation for the interaction of permanent dipoles in solution[29]. Their work is unique in that it allows the *a priori* calculation of the free energy of interaction based on the knowledge of the solute dipole moment (μ) and radius (a) and the solvent's dielectric constant. It is significant that Taft's definition of a "select" solvent is close to the concept of a non-

hydrogen-bonding polar solvent elaborated by Keller *et al.*[14]. Taft's definition, however, excludes aromatic and halogenated solvents.

The objective of this work was to investigate whether Taft's π^* polarity scale is correlated with commonly used chromatographic measures of retention such as Snyder's ε^0 scale for adsorption on alumina, and estimates of orientation solubility parameters. Although purely dipolar interactions are reasonably selective and therefore chromatographically more interesting than dispersion interactions, it is perhaps even more important to be able to estimate the strength of dipole forces to be better able to discern the contribution of very selective forces to the net intermolecular interaction. The present approach is evidently of little utility in reversed-phase liquid chromatography since these methods rely upon the use of mixed solvents which invariably contain water. It should find its greatest utility in gas–liquid chromatography (GLC).

RESULTS AND DISCUSSION

As stated above, Taft has pointed out the existence of a linear relationship between the π^* polarity value of "select" solvents and a function, termed Θ, of the solvent's dielectric constant. This relationship is obtained from a model which allows the calculation of the electrostatic contribution to the chemical potential of a dipole. Basically, the dipole is assumed to exist in a spherical cavity of radius a, defined by the solute size. The dielectric constant within the cavity is taken as exactly unity. Outside the cavity the dielectric constant is allowed to asymptotically approach the bulk dielectric constant D according to a specific but herein irrelevant relationship given by Block and Walker[28].

By Kirkwood's approach, the work (W) and thus the assumed free energy of charging of a point dipole is given by the equation:

$$W = \frac{-1}{2} \frac{\mu^2}{a^3} \Theta(D) \tag{4}$$

where μ is the dipole moment of the solute (A). The function $\Theta(D)$ is given below and plotted in Fig. 1.

$$\Theta(D) = \frac{3D \ln D}{D \ln D - D + 1} - \frac{6}{\ln D} - 2 \tag{5}$$

Θ varies from 0 at D equal to 1.00, which pertains to a vacuum, to a value of 1.000 at very high dielectric constant. Note that even for a solvent as polar as water, Θ is equal to only 0.504.

A final important point is the assumption of a non-polarizable solute. Estimates indicate that this is unlikely to cause errors of greater than 20%[27]. Implicit in the above discussion is the idea that the solute cavity size is solely established by the solute. Taft points out that this is not necessarily true, particularly if the solvent has a large non-polar end[27]. It is also important to recognize at the outset that the $\Theta(D)$ is also found to be linearly related to the solvent's dipole moment[27].
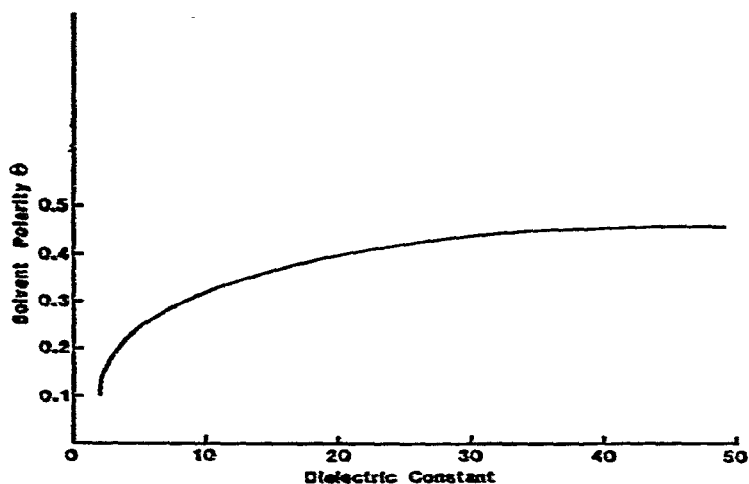
Fig. 1. Solvent polarity function plotted against solvent dielectric constant; computed according to eqn. 5.

The partition coefficient corresponding to transfer of solute from the mobile phase to the stationary phase may be obtained directly from Taft's work as follows:

$$\ln K_{eq} = \frac{1}{2} \frac{\mu_A^2}{RT \alpha^3} \left(\Theta(D_s) - \Theta(D_m) \right) \tag{6}$$

This equation can be put in terms of macroscopic properties by assuming a spherical solute molecule and a value for the voidage between molecules in the condensed state (taken here as 0.40^{30}). When the dipole moment is assigned units of Debyes, eqn. 6 (at 25 °C) numerically evaluates as:

$$\ln K_{eq} = 50.5 \frac{\mu_A^2}{V_A} \left(\Theta(D_s) - \Theta(D_m) \right) \tag{7}$$

where V_A is the molar volume of the solute. This equation is obviously of great chromatographic significance. In essence, it predicts the part of the partition coefficient that is due to the interaction of the solute's permanent dipole with the general polarity function (Θ) of the solvent. It clearly does not include dispersion interactions or acid–base interactions, nor does it encompass induction forces. Physically it corresponds to the dipole orientation solubility parameter (δ_o) as described by Karger et al.[15]. However, eqn. 6 agrees with the observation of Karger et al.[15] that the strength of a solute's dipole–dipole interaction is proportional to its dipole moment. We believe that eqn. 6 and its roots in Block and Walker's work is the fundamental explanation for their observation. As will be seen later, eqn. 6 can be used to predict the slope of the relationship between free energy of transfer and solvent–solute properties, whereas a numerical value of the slope is not predicted by Karger's[15] entirely empirical correlation of δ_o against μ but is obtainable a posteriori. The physical and mathematical formalism used to obtain eqn. 6 is very different from that

which is used in solubility parameter theory. It is very important to note that the interaction is not of the geometric mean type. The function Θ is not proportional to the square of the solvent's dipole moment but rather, as shown by Taft[27], Θ and π^* correlate closely with a linear function of the solvent's dipole moment. If the physical reality behind eqns. 4 and 5 is correct, then permanent dipoles do not interact by geometric mean processes; consequently, the mathematical approach and the experimental values of δ_o, which are estimated by use of mathematics based on the geometric mean, are, strictly speaking, not exact. Thus, one will not be able to demonstrate complete consistency between experimental values of δ_o and the function $\Theta(D)$. It should further be noted that in the approach taken by Keller et al.[14] and Karger et al.[15,16] the orientation interaction was treated as being first-order in both the solute and solvent dipole moment. This is clearly not the case for eqns. 4 and 6, i.e., the solute dependence is the same as that predicted in their work but the solvent dependence on dipole moment is weaker.

Eqn. 4 has direct applicability to the estimation of partition coefficients for liquid–liquid chromatography. It should also be useful for comparing the relative GLC retention of two solutes of equal vapor pressure or the effect of change in stationary phase on the retention of a single solute. Although the equation is inapplicable to adsorption processes, it is interesting to compare the function Θ to Snyder's ε^0 values for adsorption on alumina.

Correlation with Rohrschneider's data for GLC

Recently, Rohrschneider reported the gas-phase partition coefficient of a set of solutes, including nitromethane, in common solvents, many of which are "select"[8]. Since nitromethane is a quintessential select solvent, we attempted to see if Rohrschneider's data would correlate with eqn. 7. The relevant data from Rohrschneider, corrected for the molar volume of the solvents as described by Snyder[9] and employed by Karger et al.[16] are given in Table II and plotted vs. Θ in Fig. 2. A correlation coefficient of 0.936 was obtained. (See Table III, line 2, for statistical results.) When Rohrschneider's data are plotted vs. π^* (see Table II), a correlation coefficient of 0.955 is obtained. Thus the experimental π^* value is only slightly superior to the theoretical Θ value. To see how good a correlation coefficient this actually is, the same set of select solvents have a correlation coefficient of 0.971 when π^* is regressed against Θ (Table III, line 1). Obviously, neither is perfect but, in the first case, recalling the definition of the correlation coefficient, over 93% of the variation in $\ln K_{eq}$ is due to changes in Θ. It should be noted that we have used data for solvents which are common to both Taft's and Rohrschneider's work, excluding the non-select solvents. Values of Θ were those reported by Taft; no attempt was made to estimate Θ values for other solvents. It is evident that a linear relationship exists between $\ln K_{eq}$ (nitromethane) and Θ as well as π^*. For nitromethane ($V = 54$ ml/mol, $\mu = 3.9$ Debye) the slope of a plot of $\ln K_{eq}$ vs. $\Theta(D)$, as indicated by eqn. 7, should be 14.2. The slope of the least squares best line is 4.5 ± 0.42. The discrepancy between the good correlation coefficient yet poor agreement between the theoretical and experimental slopes is discussed later.

We also correlated Rohrschneider's data for the partitioning of methyl ethyl ketone in a series of 17 select solvents with Θ. The correlation coefficient was only 0.634, which is much poorer than that for nitromethane. In fact, the correlation

coefficient of the partition coefficient of nitromethane *vs.* methyl ethyl ketone for these 17 solvents was only 0.666. It should be noted that the slope of a plot of ln K_{eq} (methyl ethyl ketone) *vs.* Θ was 1.55 ± 0.48 (see Table III, line 3). The theoretical slope should be 4.09. Neither methyl ethyl ketone nor nitromethane is a hydrogen-bond donor, and the solvents tested all conformed to the "select" definition. It is evident that other factors, *e.g.* dispersion (see below), must have a greater relative influence on the ketone data than on the nitromethane data. This is possible since the total change in free energy of transfer of the ketone is considerably less than that of the nitromethane.

Abboud and Taft[27] have examined the free energy of transferring the extremely polar tetramethylammonium chloride ion pair from dimethylformamide to a series of nine solvents ranging from hexane to dimethyl sulphoxide. An excellent correlation coefficient (0.999) was obtained. It is reasonable to expect a good correlation in this case since the dipole moment of the solute is extraordinarily large, thus permanent dipole interactions would overwhelm dispersion processes. The total change in transfer free energy is nearly 18 kcal/mol in this case but only 1100 and 830 cal/mol for nitromethane (Table II) and methyl ethyl ketone, respectively. However, no comparison of the experimental and the theoretical slope was made.

The molar volume of tetramethylammonium chloride has been reported[31] as 107 ml. Using this value and a conservative estimate of the ion pair dipole moments (8.5 D[27], eqn. 7 predicts a slope of 34.1, which should be compared to the value 50.1 observed by Abboud and Taft[27]. The discrepancy between predicted and observed slopes in this case is not as great and may well be due to the error in estimating α from the molar volume since the charges in the dipole are probably closer together than estimated from $\overline{V}_A$. Secondly, the quadrupole contribution to the transfer energy may be as large as 10% in this case[32].

Correlation with orientation solubility parameters

As explained above, the relationship between the Θ polarity function and the orientation solubility parameter (δ_o) cannot be rigorously valid owing to the requirement for a geometric mean interaction. Nonetheless it is interesting to ignore such difficulties and examine the formal relationship between Θ and δ_o. Since Θ represents only interaction between permanent bond dipoles, we will relate it to the *orientation* solubility parameter (δ_o). Let us imagine a perfectly non-polarizable, dipolar molecule. By this definition, the dispersion parameter (δ_a) is exactly zero, thus, by the definition of the solubility parameter, the internal energy which may be taken as the molar energy of vaporization, ΔE^V, will be

$$-\Delta E^V = \overline{V}\,\delta_0^2 \tag{8}$$

where $\overline{V}$ is the molar volume of the pure liquid.

This may be equated with the work needed to transfer 1 mol of A to an ideal gas phase (see eqn. 4) from a solution of pure A, thus

$$\left(\delta_0^A\right)^2 = \frac{1}{2}\frac{\mu_A^2}{\alpha^3\,\overline{V}_A}\,\Theta(D_A) \tag{9}$$

TABLE II

PROPERTIES OF COMMON SOLVENTS[a]

Solvent	Type[b]	V^c	μ^d	π^{**}	$\Theta(D)^f$	$\ln K_{FIM}^g$	$\ln K_{MEK}^h$	$\delta_{s,ih}^{i,l}$	$\delta_{s,nsp}^{i,l}$	$\delta_p^{i,k}$	$\delta_p^{i,l}$	ε^m
1 Hexane	S	130	0	−0.081	0.103	4.25	4.67	0	0	0	0	0
2 Heptane	S	146	0	0.081	0.104	—	—	0	0	0	0	0
3 Cyclohexane	S	108	0	0.000	0.112	4.14	4.59	0	0	0	0	0.4
4 Triethylamine	S	140	0.7	0.140	0.138	4.81	4.98	0.10	0	—	—	—
5 Di-n-butyl ether	S	170	—	0.239	0.172	4.92	5.00	—	—	—	—	—
6 Diisopropyl ether	S	108	1.1	0.271	0.204	5.01	5.05	0.71	1.0	2.38	—	0.28
7 Diethyl ether	S	105	1.2	0.273	0.219	5.09	5.02	0.85	5.76	12.8	1.96	0.38
8 Carbon tetrachloride		97	0	0.294	0.127	—	—	0	0	0	0	—
9 Propanol		75	—	0.534	—	—	—	—	6.76	63.5	—	—
10 Toluene		107	—	0.535	—	—	—	—	0	0	0	—
11 Ethanol	S	59	1.9	0.540	—	—	—	—	11.56	18.3	0	0.58
12 Ethyl acetate	S	98	1.9	0.545	0.260	5.71	—	2.91	16	20	6.76	0.58
13 Dioxane		86	—	0.553	—	—	—	—	27.04	42.6	—	—
14 Ethyl bromide	S	77	2.0	0.558[n]	0.313	5.20	5.64	6.29	9.61	18.97	2.25	0.37
15 Methyl acetate	S		—	0.56	—	—	—	—	—	—	—	0.60
16 Tetrahydrofuran	S	82	1.8	0.576	0.285	5.64	5.24	4.09	12.25	24.41	7.84	0.58
17 Methanol		41	—	0.586	—	—	—	—	24.01	33.9	—	—
18 Benzene		89	0.0	0.588	0.132	—	—	0	0	0	0	—
19 Methyl ethyl ketone	S	90	2.7	0.674	0.383	5.80	—	10.3	22.1	39.13	19.36	0.51
20 Acetone	S	74	2.9	0.683	0.394	5.81	5.32	18.0	26.0	46.4	21.0	0.56
21 Chlorobenzene		102	1.6	0.709	0.252	—	—	1.85	3.61	9.1	4.41	—
22 Acetonitrile	S	53	3.7	0.713	0.446	5.85	5.19	64.7	70.6	104	77.4	0.71
23 Anisole		109	1.3	0.734	0.219	—	—	—	4.45	11.69	—	—
24 Cyclohexanone	S	104	3.1	0.755	0.367	5.75	5.26	0.93	—	—	—	—
25 Chloroform		81	1.3	0.760	0.232	—	—	—	9.0	17.1	7.3	—
26 Bromobenzene		105	—	0.794	—	—	—	1.78	2.25	4.5	—	—

No.	Solvent	[b]	V[c]	μ[d]	π^*[e]	Θ[f]	[g]	[h]	δ_p^2[i]	[j]	[k]	[l]	[m]
27	1,2-Dichloropropane		79		0.807	—	—	—	—	17.6	25.8	—	—
28	Propionitrile	S	71	4.0	0.387ⁿ	0.419	—	—	41.8	43.6	68.4	49.0	—
29	Nitromethane	S	54	3.5	0.848	0.448	—	5.19	55.6	68.9	113	84.6	0.64
30	Nitropropane		88	3.6	0.860ⁿ	0.408	—						0.53
31	Nitroethane	S	71	3.7	0.860ⁿ	0.425	5.78	5.32	34.4	36.0	68.1	57.8	—
32	Pyridine		81	2.2	0.867	0.342	—	—	7.51	14.4	32.4	18.5	—
33	Hexamethylphosphoramide	S	176	—	0.871	—	—	—	—	11.6	40.1	—	—
34	γ-Butyrolactone	S	77		0.873	—	—	—	—	51.8	103	—	—
35	Dimethylformamide	S	77	3.8	0.875	0.444	6.03	5.22	32.2	38.4	76.4	44.9	—
36	Dimethylacetamide	S	92	3.8	0.882	0.447	6.09	5.27	22.7	22.1	48.3	31.4	—
37	2-Methylpyrrolidone	S	76	4.1	0.921	0.433	6.09	5.21	37.1			72.3	—
38	Ethylene glycol		56		0.932	—	—	—	—	46.2	65.8	—	—
39	Dimethyl sulfoxide	S	71	3.9	1.00	0.467	6.00	4.95	42.0	37.2	72.5	64.0	0.62
40	Nitrobenzene		103	3.9	1.029	0.440	—	—	18.8	13.0	33.9	17.6	—

ᵃ These solvents are those which are common to Taft's list of π^* values and either Karger et al.'s[16] or Barton's[33] list of solubility parameters. Only select solvents were tested in any correlation except where indicated in the text.

ᵇ The solvents indicated with an S in this column are defined as being select by Abboud and Taft[27].

ᶜ The molar volume of the solvent (ml/mol).

ᵈ The dipole moment in Debyes from ref. 26, except as indicated.

ᵉ The Taft π^* value from ref. 25.

ᶠ The value of the Θ function for the solvent from ref. 27.

ᵍ The natural logarithm of the mole fraction equilibrium constant for the partitioning of nitromethane between the gas phase and the indicated solvent, from ref. 8.

ʰ The natural logarithm of the mole fraction equilibrium constant for the partitioning of methyl ethyl ketone between the gas phase and the indicated solvent, from ref. 8.

ⁱ The theoretical value of δ_p^2, computed from eqn. 10 (cal/ml).

ʲ The experimental orientation solubility parameter (cal/ml), from ref. 15.

ᵏ The experimental polar solubility parameter computed from eqn. 12 with the data of ref. 14.

ˡ The experimental polar solubility parameter, from ref. 33.

ᵐ The solvent strength for alumina as an adsorbent, from ref. 3.

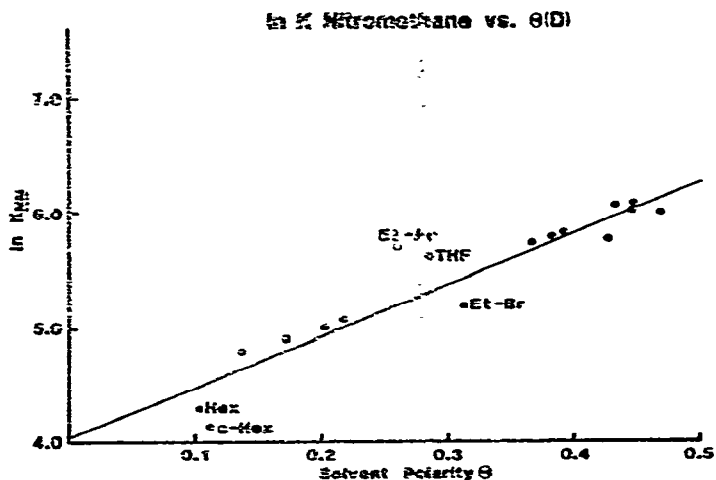ⁿ Estimated from Taft's correlation of dipole moment with π^*.

Fig. 2. Plot of logarithm of mole fraction partition coefficient of nitromethane against solvent polarity function (Θ). The number on each point refers to the list of solvents in Table II.

Since eqn. 4 and, therefore, eqn. 9, are inherently based on the assumption of a spherical solute, we proceed, as before, to replace a^3 with the molar volume of the solute. When μ and δ are assigned units of Debyes and $(cal/ml)^{1/2}$ respectively, we obtain

$$\left(\delta_{0,th}^{A}\right)^2 = 2.98 \cdot 10^4 \left(\frac{\mu_A}{V_A}\right)^2 \Theta(D_A) \tag{10}$$

This equation may be used to compute a theoretical value of the orientation solubility parameter (designated $\delta_{0,th}$) which can then be compared to experimental values ($\delta_{0,exp}$) such as those compiled by Barton[33] based on the homomorph approach, and those based on the more recent approach of Keller et al.[14]. In order not to be misleading, it should be pointed out that Karger et al.[15] empirically found that their δ_0 values did correlate with the same explicit dependence on the solvent's dipole moment and molar volume. Their approach did not, however, yield any method for the a priori prediction of the slope of a plot of δ_0 vs. μ_A/V_A, nor did it encompass the dependence of δ_0 on the solvent's dielectric constant.

The results are summarized in Table III and plotted in Fig. 3. It should be noted that the correlation was conducted in terms of the square of the solubility parameter so that the scale would be linear in energy and therefore comparable to the scale used in Fig. 2. This has the consequence that large values of δ_0 are weighted very heavily. We consider this to be a fair basis for comparison, particularly since the $\delta_{0,exp}$ values are estimated from differences in large quantities[14] and thus small values tend to be very imprecise. Secondly, when δ_0 are small, non-polar processes are dominant.

Hildebrand et al.[11] indicate that one can expect an internal consistency amongst solubility parameters which is no better than some fraction of RT, i.e. of the thermal energies; in their work the value 1/5 is chosen arbitrarily. This amounts to $\pm$ 120 cal/mol at room temperature. For a species with V of 75 ml/mol this

TABLE III

RESULTS OF VARIOUS CORRELATIONS

A conventional (slope, intercept) unweighted linear least-squares program was used except where indicated. All solubility parameters are from ref. 14 except where indicated. n = Number of data pairs in the correlation.

Correlation (y vs. x)	n[i]	Correlation coefficient	Slope ± S.D.	Intercept ± S.D.
1 Θ vs. π^*	17	0.970	0.36 ± 0.15	0.12 ± 0.15
2 ln K_{NM} vs. Θ	18	0.936	4.5 ± 0.4	4.0 ± 0.14
3 ln K_{MEK} vs. Θ	17	0.666	1.55 ± 0.48	3.65 ± 0.4
4 $(\delta_{o,exp})^2$ vs. $(\delta_{o,th})^2$[i]	17	0.972	1.02 ± 0.06	3.9 ± 1.8
5 $(\delta_{o,exp})^2$ vs. $(\mu/V)^2$[i]	17	0.979	(1.4 ± 0.07) · 10^{+4}	(2.5 ± 1.6) · 10^{-4}
6 $(\delta_{o,exp})^2$ vs. $(\delta_{o,th})^2$[i,iii]	17	0.984	1.11 ± 0.05	0[iii]
7 $(\delta_{o,exp})^2$ vs. $(\mu/V)^2$[i,iii]	17	0.975	(1.48 ± 0.06) · 10^{-4}	0[iii]
8 δ_e^2 vs. $(\delta_{o,th})^2$[i]	16	0.963	1.60 ± 0.12	11.6 ± 3.5
9 δ_e^2 vs. δ_e^2[i]	15	0.973	0.82 ± 0.05	−7.9 ± 3.2

[i] Data are from ref. 14.

[ii] This is a correlation of $\delta_e(y)$ from ref. 30 with $\delta_e(x)$ computed from the data in ref. 14.

[iii] A modified unweighted least-squares program which forces a zero intercept was employed.

amounts to an uncertainty of ± 0.8 (cal/ml)$^{1/2}$ at δ equal to 1 and only ± 0.2 at δ equal to 4. Thus there is good reason to rely on the small δ values less heavily than on the larger values.

We note from Table III that the correlations of $(\delta_{o,exp})^2$ vs. $(\delta_{o,th})^2$ and against $(\mu/V)^2$ are both very good. Indeed, the patterns of signs of the residuals for both correlations are identical. One could argue that the term Θ in eqns. 9 and 10 is only responsible for a small part of the correlation and that the dominant effect is due to
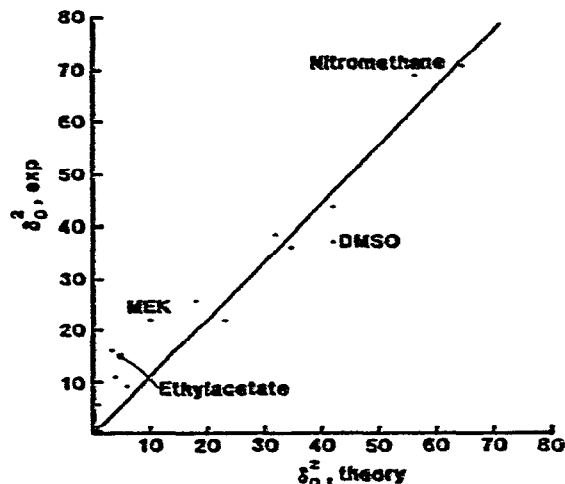

Fig. 3. Comparison of experimental and theoretical orientation solubility parameters. Experimental data are from ref. 14 and theoretical data are computed from the data in Table II. Note that solubility parameters are squared.

the term $\mu/\bar{V}$, and that perhaps the Θ function is really rather trivial. It should also be noted that both correlations yield a significant positive intercept. We felt that the use of a two-parameter (slope, intercept) fit might not be valid in view of the fact that both eqn. 10 and simple proportionality between $(\delta_{o,exp})^2$ and $(\mu/\bar{V})^2$ predict a zero intercept which is supported by all the data for totally non-polar molecules (see Table II). The regression was re-run, using a least squares program that forced a zero intercept. In this case the correlation vs. $(\delta_{o,th})^2$ produces a slightly better correlation coefficient than does the correlation $(\mu/\bar{V})^2$. The improvement is statistically insignificant at the 90% confidence level.

It should be noted as stated above that Karger et al.[15] observed that δ_o was closely correlated with $\mu/\bar{V}$, thus the correlation is not surprising. Abboud and Taft[27] have shown that Θ strongly correlates with a linear function of dipole moment. Owing to the presence of a large intercept in the correlation of Θ vs. μ, eqn. 10 actually predicts a cubic dependence of δ_o at high dipole moment but only a quadratic dependence at low dipole moment. At present, there is too much scatter in the data to disclose any such non-linearity.

We believe that the most important point in this work is not the prediction of the dependence of δ_o on $\mu/\bar{V}$ but the fact that *we are able to predict the correct slope* of the relationship. As indicated by the data of Table III, the slope of $(\delta_{o,exp})^2$ vs. $(\mu/\bar{V})^2$ is $1.4 \cdot 10^{-4}$ (line 5, Table III) whenever the slope of $(\delta_{o,exp})^2$ vs. $(\delta_{o,th})^2$ is 1.02 (line 4, Table III). We believe that the ability of eqn. 4, which includes $\Theta(D)$, to successfully predict the correct slope is the strongest argument for its use and the importance of the term $\Theta(D)$.

To a certain extent this excellent agreement is unexpected in view of the factor of 4 discrepancy in the observed and the theoretical slope of the plot of $\ln K_{eq}$ vs. Θ shown in Fig. 2.

Part of the difficulty may be due to the use of a sphere to represent the shape of all the solutes. Meyers[34] has found that the correlation between boiling temperature and molar volume can be greatly improved by taking molecular shape into account. Nonetheless, it is difficult for this alone to reconcile the error of a factor of 4 in the slope of the data of Fig. 2 with the fact that eqn. 10 underestimates δ_o of nitromethane by only 25%.

The data of Fig. 3 obviously apply only to orientation interactions. In contrast, the data of Fig. 2 necessarily involve other types of interaction, notably dispersion and induction. Karger et al.[15] have presented a model for GLC in terms of the interactions of the individual components of the solubility parameters of any two molecules. When their approach is applied to a non-hydrogen-bonding pair of solute (A) and solvent (S) molecules, one obtains:

$$-RT \ln K_{eq} = \bar{V}_A [\delta_S^2 - 2\delta_{d,A} \cdot \delta_{d,S} - 2\delta_{o,A} \cdot \delta_{o,S} - 2\delta_{in,A} \cdot \delta_{d,S} - 2\delta_{d,A} \cdot \delta_{in,S}]$$
$$(11)$$

One can show that a correlation exists for the available data between the term $\delta_{o,A} \cdot \delta_{o,S}$ and the sum of all other terms in brackets in eqn. 11. In fact, the correlation coefficient (-0.967) indicates an inverse dependence. Obviously, the low slope of the data of Fig. 2 is due to a cancellation of terms. We felt that this might reflect a correlation between δ_d and δ_o for the solvents tested. No significant correlation exists

($\varrho = -0.067$). At this time, we do not know the physical source of the correlation which, nonetheless, is statistically real for this data set.

Clearly, the effect of dispersion and induction shows up in Rohrschneider's partition coefficients but, owing to the way δ_0' is defined and its direct physical relationship to eqns. 4 and 10, other factors are excluded. Thus, the error in the predicted slope of the data of Fig. 2 is due to the presence of other factors in the data, and the accuracy of the slope of Fig. 3 is due to their successful exclusion from experimental δ_0 values.

Several other correlations were tested for the sake of completeness. The total *polar* solubility parameters for the select solvents were computed from literature data according to the equation:

$$\delta_\varrho^2 = \delta_0^2 + 2\delta_{in} \cdot \delta_d \tag{12}$$

Since the inductive solubility parameter must also depend[16,33] upon $\mu/\bar{V}$, we correlated $(\delta_{o,th})^2$ with the total experimental polar solubility parameters. As Table III (line 8) indicates, the correlation coefficient decreases slightly but the slope increases quite significantly to 1.60 ± 0.12. The polar solubility parameter data of Karger *et al.*[15] are correlated against the polar solubility parameters obtained from Barton[33]. It is evident (Table III) that the correlation between experimental measures of the same parameters are no better than the *a priori* prediction from eqn. 10. In fact, the slope of this regression is 0.82 ± 0.05. The two experimental polar solubility parameter scales are not completely consistent. We should point out that for non-polar hydrocarbons the refractive index method of predicting δ_d was only precise to within ± 0.4 (cal/ml)$^{1/2}$. Obviously it must be assumed that the correlation of δ_d with refractive index holds up even for polar compounds. This may not be entirely valid.

Correlation with Snyder's adsorbent polarity scale

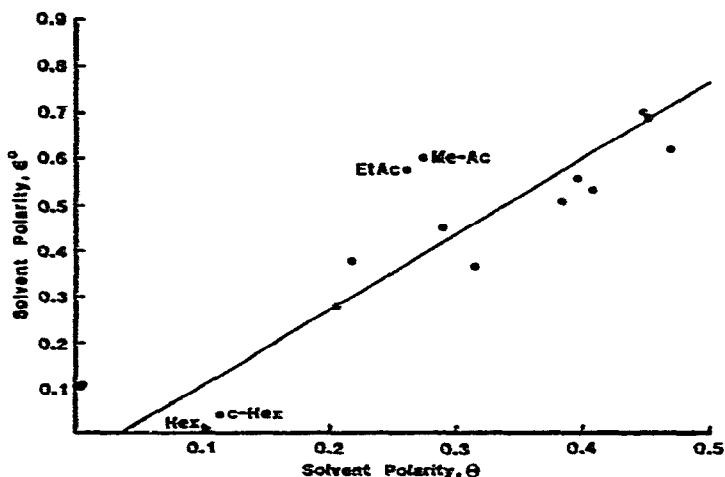Fig. 4 is a plot of Snyder's solvent strength parameter ε^0 *vs.* Θ for 15 solvents

Fig. 4. Plot of adsorption chromatography solvent strengths parameters against solvent polarity function. All data are from Table II.

ranging in polarity from hexane ($\varepsilon^o = 0$; $\Theta = 0.103$) to acetonitrile ($\varepsilon^o = 0.50$; $\Theta = = 0.446$). It is obvious that the correlation is not nearly as good as that in Figs. 2 and 3. The correlation coefficient is only 0.930. When the three non-polar hydrocarbons are deleted from the line, the correlation coefficient drops to only 0.69. It is not surprising that the Θ function does not adequately represent the interactions of solvent molecules with the surface of an adsorbent. Obviously there are enormous differences in the geometry of the allowable interactions. Secondly, the Θ polarity function only accounts for orientation interactions. Karger et al.[16] have presented convincing data that electron pair acceptor sites on alumina are very important in adsorption chromatography. The chief reason why a correlation coefficient as high as 0.92 is obtained in this case is because dispersion interactions which are associated with non-polar groups are relatively unimportant for   sorption on alumina.

CONCLUSIONS

At this point, we believe that the Θ polarity function described by Taft, and the related π^* polarity scale, have considerable importance in chromatography. It is clear that none of the correlations of the properties of select solvents described in this work is quite as good as those found by Taft (see Table I). This can be attributed to the fact that partition equilibria are governed by the sum of all intermolecular forces on all atoms in a molecule. In contrast, solvent effects on reaction rates, chemical equilibria between two species or photon absorption tend, to a first approximation, to be localized about those groups on the molecule which participate in the chemical reaction or are responsible for photon absorption. In our view the Taft π^* polarity scale is rather sensitive to dipolar interactions and rather insensitive to dispersion interactions. This concept is supported by the linear relationship between π^* and Θ since Θ is not strongly dependent on molecular polarizability but is closely related to the solvent's dipole moment. Chromatographic retention is evidently very sensitive to both dispersive and polar forces. It would seem that net retention in select solvents could be better described by a combination of dispersion interaction via δ_d and Taft's π^* or by the Θ function as a measure of permanent dipole interactions.

ACKNOWLEDGEMENTS

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