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# Measurement of solute dipolarity/polarizability and hydrogen bond acidity by inverse gas chromatography

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ABSTRACT

Solvatochromically based linear solvation energy relationships (LSERs) have been studied for more than ten years and been applied to the study of a very wide variety of chemical phenomena. During the past several years they have been used to explore retention processes and characterize gas chromatographic stationary phases. However, the general application of this method is limited by the complex and tedious methods needed to measure the explanatory variables and by the limited accuracy of the *a priori* parameter estimation rules. In this paper we have investigated the use of retention data for a wide variety of solutes on more than a dozen very different gas chromatographic stationary phases, including a number of extremely basic phases. These data are the basis for a method of rapidly estimating two of the explanatory variables commonly encountered in solvatochromic LSERs. Using the above approach, the polarity/polarizability parameters and the hydrogen bond donor acidity parameters for more than 200 compounds have been estimated. The results suggest that these two parameters can be estimated with a precision, and perhaps accuracy, at least as good as the more time-consuming methods. We have demonstrated that the Martin equation and LSER equations based on these parameters are compatible. Finally we have shown for the first time that the coefficients of the LSER, as required by basic theory, are proportional to the liquid phase solvatochromic parameters.

INTRODUCTION

When Kamlet and co-workers initiated their studies [1–3] of linear solvation energy relationships (LSERs), their goal was to explore how a solvent influences a property (denoted as $XYZ$) of a single solute. Their earliest studies were concerned with the effect of solvent on spectroscopic properties of a carefully chosen set of solutes. All of their initial work involved the $\pi \rightarrow \pi^*$ and $p \rightarrow \pi^*$ electronic spectra of difunctional aromatic probe solutes, N,N-dimethyl-*p*-nitroaniline being a typical solute. By choice of solute and spectroscopic methodology they hoped to elucidate the type and relative strength of the intermolecular interactions. Their solvatochromic comparison method [4–6], is based on the idea that by suitable choice of probe and reference solutes, and spectroscopic method a solvent's ability to stabilize a solute by dipolar, hydrogen bond donor, and hydrogen bond acceptor processes could be separated and measured. This work culminated in a set of three solvent parameters: the $\pi^*$, $\alpha$ and $\beta$ values for more than 200 liquids [7]. A solvent's $\pi^*$ value is a measure of its

ability to stabilize a neighboring dipole by virtue of the dipole–dipole and dipole–induced dipole forces which exist between the dipolar solute (test probe) and the solvent. The $\pi^*$ scale is defined to be zero for cyclohexane and unity for dimethyl sulfoxide (DMSO) at room temperature. The $\alpha$ and $\beta$ scales represent the ability of a solvent to donate and accept hydrogen bonds from a solute. For various spectroscopic properties of a solute in a series of solvents Kamlet and Taft proposed the following specific LSER:

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta \tag{1}$$

The $\pi^*$ parameter was initially proposed as a measure of the solvent's ability to interact with a solute via dipole–dipole interactions. For the class of select solvents, that is, those which are aliphatic, monodipolar and aprotic, the measured $\pi^*$ values correlate with a simple function of solvent dielectric strength and is a linear function of the molecular dipole moment [8]. $\pi^*$ can be used to correlate results obtained in aromatic and poly-halogenated solvents provided that it is replaced with a corrected value as shown in eqn. 2.

$$XYZ = XYZ_0 + s(\pi^* - d\delta) + a\alpha + b\beta \tag{2}$$

When modified by the $d\delta$ term, $\pi^*$ can then be used to correlate a wide variety of properties, not just spectroscopic properties, of select, aromatic and polyhalogenated solvents [9].

It is now widely recognized that the correction ($d\delta$) is needed because $\pi^*$ also includes considerable contributions from the solvent's own polarizability [10] and that the $\pi^*$ for a very wide variety of solvents can be correlated with functions that incorporate both the dielectric strength and refractive index of the solvent [8,11,12]. As an example of the dependence of $\pi^*$ on the solvent polarizability we note that $\pi^*$ systematically varies from $-0.08$ for $n$-pentane to $0.08$ for $n$-hexadecane [13] despite the fact that the dipole moments for these solvents are essentially zero. Thus, whenever the property under study results from a different "mix" of solvent dipolarity and polarizability than the spectroscopic processes used to measure $\pi^*$, a polarizability correction term ($d\delta$) is required.

The various fitting coefficients in eqns. 1 and 2 are very important. As Kamlet and co-workers pointed out very early in his work [1,2] both the signs and magnitudes must make chemical sense in order for a given regression to be accepted even if a statistically good correlation is observed. This requirement provides protection from a tendency to reach false conclusions as to the existence of causative relationships.

Since $\pi^*$ represents the solvent's ability to interact with and stabilize a probe's (solute's) dipole via electrostatic interaction one expects that the coefficient $s$ in the LSER equations should be related to the extent to which dipolar forces are involved in $XYZ$. Thus if the probe is non-polar or the process is not sensitive to dipolar interaction one expects $s$ to be zero or small. Rutan et al. [14] demonstrated this for the transfer of small solutes from the gas phase to a wide variety of solvents. In that work $s$ was observed to be linearly related to the solute's monomer $\pi^*$ value (see below). Similarly if the probe is a weak hydrogen bond base or if the process under study is not sensitive to the solvent's hydrogen bond acidity ($\alpha$) then the coefficient $a$ in eqns. 1 and

2 will be zero or small. This concept was used by Kamlet et al. [6] in the development of solvent $\pi^*$ values for very strong hydrogen bond donor solvents and was applied by Cheong and Carr [15] to measure the $\pi^*$ of mobile phases used in reversed-phase liquid chromatography. Clearly if one wants to use some property to measure a solvent's $\alpha$ value then the probe molecule must be a strong hydrogen bond base. Conversely if one wants to measure a probe's ability to donate a hydrogen bond the solvent must be a good acceptor. As a general rule the coefficients $a$ and $b$ complement $\alpha$ and $\beta$ as they appear in eqns. 1 and 2. That is the coefficient of $\alpha$ ($a$) depends on the probe's $\beta$ and the coefficient of $\beta$ ($b$) depends on the probe's $\alpha$.

For present purposes among the more relevant tests of the solvatochromic LSER methodology is the investigation of gas–liquid partition equilibria [14–16]. Despite some interesting preliminary results it is now clear that the LSERs given in eqns. 1 and 2 are incomplete when applied to gas–liquid transfer processes. In the vast majority of prior LSER studies the processes involved only very minimal perturbation of the structure of the liquid. In contrast, many models of gas solubility invoke, at the outset, a "cavity formation process" [17,18] which is completely absent in eqns. 1 and 2. Second, it is generally accepted that London dispersion is invariably the major type of interaction in condensed phases [19]. Such dispersion interactions are entirely negligible in gases relative to liquids and thus there is no opportunity for them to cancel in a gas-to-liquid transfer process. Although it can be argued that London forces will be reflected to a limited extent in $\pi^*$, a single parameter simply cannot accurately model dipolar, polarizability and dispersion forces. Consequently the LSER model had to be expanded to incorporate a non-solvatochromic parameter in order to model cavity formation. The Hildebrand solubility parameter ($\delta_H^2$) was chosen on a purely ad hoc basis. Qualitative and quantitative agreement was observed [14,16]. In subsequent work in which a number of polar solutes were studied in a large number of solvents the cavity term was canceled, as was some dependence on solute–solvent dispersion interactions by examining the ratio of the gas–liquid partition coefficient of the solute of interest ($K_i$) to that of an n-alkane of the same size ($K_{alkane}$). That is, the following LSER was used:

$$XYZ = \log (K_i/K_{alkane}) = XYZ_0 + s(\pi^* - d\delta) + a\alpha + b\beta \qquad (3)$$

In later work Rutan et al. [20] showed that eqn. 3 had to be amended in order to handle protic self-associated solvents.

$$\log (K_i/K_{alkane}) = XYZ_0 + s(\pi^* - d\delta) + a\alpha + b\beta + h\alpha\beta \qquad (4)$$

After the development of the above three solvent scales the fundamental concept was inverted. That is, the possibility that a conceptually similar approach could be used to assess solute-to-solute variations of some property in a fixed solvent was proposed. This is closely related to the goals of quantitative structure activity relationships (QSAR) which has found considerable currency in the design of drugs, prediction of toxicity, biological activity, environmental transport and chromatographic retention [21]. This, in fact, was a very bold step. Simply stated the measured properties of the pure bulk species were used to represent the dipolar and hydrogen bond forming interactions of the same molecule acting as a very dilute species in all environments.

This step is clearly based on the assumption that the properties in question are independent of media. One of the earliest tests of this idea was its use in correlating retention in reversed-phase liquid chromatography [22–24]. It was later used to study octanol–water partition coefficients, and solubility in water [25]. The LSER used in liquid–liquid transfer "solute" studies is:

$$XYZ = XYZ_0 + mV_2/100 + s(\pi_2^* + d\delta) + a\alpha_2 + b\beta_2 \tag{5}$$

The subscript 2 denotes a solute property and $XYZ$ is now a solute property. Also note the incorporation of a solute size ($V_2/100$) parameter to scale the cavity formation process in the condensed phases. The $V_2$ term in eqn. 5 is the complement of the $\delta_H^2$ parameter used in solvent studies.

Kamlet found that the solvatochromically defined *solvent* parameters could be used as the corresponding solute parameters provided that the species in question did not self-associate in the pure liquid state. For self-associating species, for example alcohols, the solvatochromic parameters had to be empirically modified so as to better fit the property under study. These modifications were justified based on the work of Abboud and co-workers [26,27] which shows that alcohol dimers are simultaneously both stronger hydrogen bond donors (HBD) and acceptors in the bulk phase than are alcohol monomers. While the idea that species which self-associate in the pure liquid phase should have different parameters when the same species acts as a monomeric, infinitely dilute species is chemically rational, it reveals a dilemma. The situation is best made clear with the following example. The $\alpha$ and $\beta$ of methanol acting as a solvent are 0.93 and 0.62, respectively. In contrast, when methanol acts as a monomer (m) species, Kamlet [25] assigned the $\alpha_m$ and $\beta_m$ as 0.35 and 0.42. Similarly Abraham established, via hydrogen bond formation equilibrium constants (see below), that the values of $\alpha_2^H$ and $\beta_2^H$ are equal to 0.37 and 0.41 for methanol. Suppose we consider the properties of methanol as a dilute species in ethanol as a solvent. Clearly the chemical environment of a methanol monomer in ethanol is quite similar to that in pure bulk methanol. Which parameters should be used to represent the properties of a methanol monomer in this media? This suggests that even the *relative* hydrogen bond acidity and basicity scale may vary with media and thus no constant ranking is possible. A comprehensive list of solute interaction parameters and an extensive list of parameter estimation rules are available [25].

The tremendous importance of hydrogen bonding interactions in chemistry and biology has led Abraham and his co-workers [28,29] to develop a scale of relative hydrogen bond acidities ($\alpha_2^H$) and basicities ($\beta_2^H$) for dilute species. These are based on measurements of hydrogen bond equilibrium constants of a wide variety of substances in carbon tetrachloride and 1,1,1-trichloroethane. With a few notable exceptions, reasonably but not completely, general scales of hydrogen bond acidity and basicity are possible [30]. This results because for many pairs of hydrogen bond donors and acceptors the ratio of electrostatic and covalent bonding in hydrogen bond formation is constant and front strain is minimal.

A series of papers [31,32] have appeared on the study of the adsorption of dilute gases in polymers, on carbon adsorbents and in gas chromatographic (GC) stationary phases. In such studies the overwhelming solute–solvent interaction is dispersion and the use of a simple dependence on solute volume inadequately represents this process.

Abraham and co-workers [33,34] have shown that dispersion interactions and cavity formation processes can be handled by using the logarithmic gas–liquid partition coefficient in $n$-hexadecane (denoted as log $L^{16}$) as an explanatory variable to simultaneously model both processes.

$$XYZ = XYZ_0 + l \log L^{16} + s\pi_2^* + d\delta_2 + a\alpha_2 + b\beta_2 \qquad (6)$$

This approach is clearly approximate. In our recent study [35] of retention on a set of eight capillary gas chromatographic columns wherein the stationary phases ranged from a very non-polar permethyl silicone polymer to a very polar polyethylene glycol (Carbowax) phase we showed that eqn. 6 failed to accurately model retention. However, we were able to achieve a fit almost as precise as the random error in the measured property by using retention data on both a non-polar and a very polar reference column along with the solvatochromic parameters ($\pi_2^*$, $\delta_2$, $\alpha_2$, $\beta_2$) as the explanatory variables. This led us to believe the parameters we were using in that study were incorrect and that a need to develop new LSER parameter scales exists. We believe that the double reference column approach worked simply because the use of a polar reference column reduced the strength of the dependence on the interaction parameters and consequently inaccuracies in these parameters had a smaller effect on the quality of the fit.

In the present work we investigated the possibility of using eqn. 6 for the estimation of a new solute $\pi_2^*$ and $\alpha_2$ parameter, herein designated as $\pi_2^{*,C}$ and $\alpha_2^C$. The superscript C indicates that the parameters are derived from chromatographic data. Because there are few highly acidic yet weakly basic phases in our data base we felt it premature and too complex to estimate a new $\beta_2^C$ parameter. In order for this approach to work one must include chemically diverse stationary phases to obtain reliable results. Clearly it is important that retention data on as many columns as possible be linearly independent.

EXPERIMENTAL

Three different data bases (A,B,C) were used in this work. The first data base (A) is a set of capacity factors ($k'$) for 53 highly variegated compounds that span an extremely wide range in chemical characteristics on 8 common capillary columns ranging from a methyl silicone oil to polyethylene glycol. The details of this data base have been published [35] (see the last column in Table I). The second data base (B) includes the capacity factors of 87 compounds, which includes all of the solutes in data base A, on 6 very basic phases. These basic phases are: tris-(2-ethylhexyl) phosphate (TEHP), trioctyl phosphine oxide (TOPO), N,N-diethyldodecylamide (DEDA), methyl dioctylamine (MDOA), dimethyl dodecylamine (DMDA) and 4-butylpentyl pyridine (BPP). The first three phases are oxygen bases, and the last three are nitrogen bases. These compounds were chosen because they are quite basic, have low volatility and similar molecular weights. The column temperatures were different for each phase and details of this data base will be published elsewhere. The compounds in this data base are designated as B in Table I. The third data base (C) is a part of the Patte et al. [36] data base used by Abraham et al. [37] to classify various GC phases. It includes the relative capacity factors (or specific volumes) (denoted $L'$) for 166 compounds on

5 stationary phases. Those five phases are: Zonyl E 7 (ZE7), Carbowax 1540 (Carbowax), 1,2,3-tris(2-cyanoethoxy)propane (TCEP), polyphenyl ether 6 rings (PPE6) and diethylene glycol succinate (DEGS). The compounds included in this data base are designated as C in Table I.

COMPUTATIONAL METHODS

The computations were started by determining the regression coefficients of eqn. 6 with the best available estimates of the LSER parameters (see Table I). Thus we use $\pi_2^*$, $\alpha_2^H$, and $\beta_2^H$ from Abraham to initialize the first values of $\pi_2^{*,C}$ and $\alpha_2^C$. In order to minimize the effect of determinate errors in the initial estimates of the parameters on the fitting coefficients ($l$, $s$, $a$, $b$ and $d$) a zero lag adaptive Kalman filter [41] was used. This approach was chosen because it produces fitting coefficients which are much less sensitive to outliers than does conventional linear least squares analysis. However, because the Kalman filter is recursive inherently it must assume that the first few data ($k'$, $\log L^{16}$, $\pi^*$, $\alpha_2^H$, $\beta_2^H$) in a set are accurate. This must lead to some bias in the fitting coefficients due to the initial data sequences. To minimize such bias the filter was run several times with randomized data sequences. Once the fitting coefficients were obtained for all the columns (in the three data bases) the following steps were taken to achieve the final estimates of the new $\pi_2^{*,C}$ and $\alpha_2^C$ parameters.

(a) Those columns with large $s$ coefficient (greater than one) and small $a$ and $b$ coefficients were used as the basis for calculating $\pi_2^{*,C}$. Data on these columns were force-fitted to eqn. 6 by merely adjusting the $\pi_2^*$ parameters. The resulting $\pi_2^*$ values were normalized by setting $\pi_{2,\text{cyclohexane}}^* = 0$ and $\pi_{2,\text{DMSO}}^* = 1.00$, then the average over all columns with high $s$ values was taken as a first round estimate of $\pi_2^{*,C}$.

(b) The $\pi_2^{*,C}$ parameters from step $a$ were used to replace the initial $\pi_2^*$, then all the data were again regressed against eqn. 6 by using the adaptive Kalman filter procedure. The columns which gave a large $a$ coefficient and a small or negligible $b$ coefficient ($s$ is not necessary small) were chosen as the basis for calculating $\alpha_2^C$. Data on those columns were force-fitted to equation 6 by adjusting the $\alpha_2^H$ parameters. The $\alpha_2^C$ values so obtained were normalized by setting $\alpha_2^C$ (non-HBD compounds) = 0 and $\alpha_2^C$ (trifluoroethanol) = 0.57, then the average over all columns with high $a$ coefficients was taken as a first round estimate of $\alpha_2^C$.

(c) Steps a and b were repeated until no significant change was observed in either the coefficients or the parameters (2–3 cycles sufficed).

(d) Using the parameters from step c, a conventional linear least squares regression was performed for all columns. The fitting coefficients ($l$, $s$, $a$, $b$, $d$) for all the columns and the residuals [$\log k'$ (experimental) $-$ $\log k'$ (calculated)] for each compound on each column were obtained. For any compound whose residual was large on most or all of the columns, a least median analysis [41] was applied to simultaneously adjust the two parameters ($\pi_2^{*,C}$ and $\alpha_2^C$) for that specific compound to minimize the residuals on all the columns. These values constitute the final set of $\pi_2^{*,C}$ and $\alpha_2^C$.

(e) To obtain an estimate of the standard deviation in the $\pi_2^{*,C}$ and $\alpha_2^C$ from different columns, the linear least squares regression coefficients for eqn. 6 were determined and sets of $\pi_2^{*,C}$ were back-calculated from the columns which were used in step a and $\alpha_2^C$ were back-calculated from the columns used in step b.

## TABLE I

### INITIAL INPUT PARAMETERS

| No. | Compound | $\log L^{16a}$ | $\pi_2^{*b}$ | $\alpha_2^{Hc}$ | $\beta_2^{Hd}$ | $\delta_2^{e}$ | Ref.$^f$ |
|-----|----------|----------------|--------------|------------------|------------------|----------------|----------|
| 1 | Propane | 1.050 | 0.00 | 0.00 | 0.00 | 0.0 | C |
| 2 | Isobutane | 1.409 | 0.00 | 0.00 | 0.00 | 0.0 | C |
| 3 | Butane | 1.615 | 0.00 | 0.00 | 0.00 | 0.0 | C |
| 4 | Pentane | 2.162 | 0.00 | 0.00 | 0.00 | 0.0 | A,B,C |
| 5 | 2,4-Dimethylpentane | 2.841 | 0.00 | 0.00 | 0.00 | 0.0 | C |
| 6 | 2-Methylpentane | 2.507 | 0.00 | 0.00 | 0.00 | 0.0 | B,C |
| 7 | Hexane | 2.662 | 0.00 | 0.00 | 0.00 | 0.0 | A,B,C |
| 8 | 2,2,5-Trimethylhexane | 3.530 | 0.00 | 0.00 | 0.00 | 0.0 | C |
| 9 | $n$-Heptane | 3.173 | 0.00 | 0.00 | 0.00 | 0.0 | B,C |
| 10 | 3-Methylheptane | 3.510 | 0.00 | 0.00 | 0.00 | 0.0 | C |
| 11 | 2-Methylheptane | 3.480 | 0.00 | 0.00 | 0.00 | 0.0 | C |
| 12 | $n$-Octane | 3.677 | 0.00 | 0.00 | 0.00 | 0.0 | A,B,C |
| 13 | $n$-Nonane | 4.182 | 0.00 | 0.00 | 0.00 | 0.0 | B,C |
| 14 | $n$-Decane | 4.686 | 0.00 | 0.00 | 0.00 | 0.0 | A,B,C |
| 15 | $n$-Undecane | 5.191 | 0.00 | 0.00 | 0.00 | 0.0 | A,B,C |
| 16 | $n$-Dodecane | 5.696 | 0.00 | 0.00 | 0.00 | 0.0 | B,C |
| 17 | $n$-Tridecane | 6.200 | 0.00 | 0.00 | 0.00 | 0.0 | B,C |
| 18 | $n$-Tetradecane | 6.705 | 0.00 | 0.00 | 0.00 | 0.0 | A,B,C |
| 19 | $n$-Pentadecane | 7.209 | 0.00 | 0.00 | 0.00 | 0.0 | A |
| 20 | Cyclopentane | 2.426 | 0.00 | 0.00 | 0.00 | 0.0 | B |
| 21 | Cyclohexane | 2.913 | 0.00 | 0.00 | 0.00 | 0.0 | A,B,C |
| 22 | Cycloheptane | 3.543 | 0.00 | 0.00 | 0.00 | 0.0 | B |
| 23 | Propene | 0.946 | 0.08 | 0.00 | 0.07 | 0.0 | C |
| 24 | 1-Butene | 1.491 | 0.08 | 0.00 | 0.07 | 0.0 | C |
| 25 | 1-Pentene | 2.013 | 0.08 | 0.00 | 0.07 | 0.0 | C |
| 26 | 1-Hexene | 2.547 | 0.08 | 0.00 | 0.07 | 0.0 | A,B,C |
| 27 | 1-Heptene | 3.063 | 0.08 | 0.00 | 0.07 | 0.0 | C |
| 28 | ($cis$)-2-Octene | 3.650 | 0.08 | 0.00 | 0.07 | 0.0 | C |
| 29 | 2-Ethyl-1-hexene | 3.510 | 0.08 | 0.00 | 0.07 | 0.0 | C |
| 30 | 1-Octene | 3.591 | 0.08 | 0.00 | 0.07 | 0.0 | C |
| 31 | α-Pinene | 4.200 | 0.10 | 0.00 | 0.10 | 0.0 | C |
| 32 | 1-Octyne | 3.480 | 0.20 | 0.13 | 0.20 | 0.0 | C |
| 33 | 2-Octyne | 3.480 | 0.20 | 0.00 | 0.20 | 0.0 | C |
| 34 | Methanol | 0.922 | 0.40 | 0.37 | 0.41 | 0.0 | A,B,C |
| 35 | Ethanol | 1.462 | 0.40 | 0.33 | 0.44 | 0.0 | A,B,C |
| 36 | 1-Propanol | 2.097 | 0.40 | 0.33 | 0.45 | 0.0 | A,B,C |
| 37 | 1-Butanol | 2.601 | 0.40 | 0.33 | 0.45 | 0.0 | B,C |
| 38 | 2-Methyl-1-propanol | 2.399 | 0.40 | 0.33 | 0.45 | 0.0 | B,C |
| 39 | 2-Methyl-1-butanol | 3.011 | 0.40 | 0.33 | 0.45 | 0.0 | C |
| 40 | Isopentanol | 2.885 | 0.40 | 0.33 | 0.45 | 0.0 | B,C |
| 41 | 1-Pentanol | 3.106 | 0.40 | 0.33 | 0.45 | 0.0 | B,C |
| 42 | 1-Hexanol | 3.610 | 0.40 | 0.33 | 0.45 | 0.0 | B,C |
| 43 | 1-Heptanol | 4.115 | 0.40 | 0.33 | 0.45 | 0.0 | B,C |
| 44 | 1-Octanol | 4.619 | 0.40 | 0.33 | 0.45 | 0.0 | C |
| 45 | 1-Nonanol | 5.124 | 0.40 | 0.33 | 0.45 | 0.0 | C |
| 46 | 1-Decanol | 5.628 | 0.40 | 0.33 | 0.45 | 0.0 | C |
| 47 | 1-Undecanol | 6.130 | 0.40 | 0.33 | 0.45 | 0.0 | C |
| 48 | 1-Dodecanol | 6.640 | 0.40 | 0.33 | 0.45 | 0.0 | C |
| 49 | 2-Propanol | 1.821 | 0.40 | 0.32 | 0.47 | 0.0 | A,B,C |
| 50 | 2-Butanol | 2.338 | 0.40 | 0.32 | 0.47 | 0.0 | B,C |
| 51 | 2-Hexanol | 3.340 | 0.40 | 0.32 | 0.47 | 0.0 | C |

TABLE I *(continued)*

| No. | Compound | $\log L^{16a}$ | $\pi_2^{*b}$ | $\alpha_2^{Hc}$ | $\beta_2^{Hd}$ | $\delta_2^{e}$ | Ref.$^f$ |
|-----|----------|---------------|-------------|-----------------|----------------|----------------|---------|
| 52 | 3-Hexanol | 3.440 | 0.40 | 0.32 | 0.47 | 0.0 | C |
| 53 | *tert.*-Butanol | 2.018 | 0.40 | 0.32 | 0.49 | 0.0 | A,B,C |
| 54 | 3-Methyl-3-pentanol | 3.277 | 0.40 | 0.32 | 0.49 | 0.0 | C |
| 55 | 2-Methyl-2-pentanol | 3.181 | 0.40 | 0.32 | 0.49 | 0.0 | C |
| 56 | 2-Methyl-2-heptanol | 3.990 | 0.40 | 0.32 | 0.49 | 0.0 | C |
| 57 | Prop-2-en-1-ol | 1.996 | 0.45 | 0.33 | 0.41 | 0.0 | C |
| 58 | 2-Hexenol | 3.510 | 0.45 | 0.33 | 0.41 | 0.0 | C |
| 59 | *trans*-2-Heptenol | 4.010 | 0.45 | 0.33 | 0.41 | 0.0 | C |
| 60 | *trans*-2-Octenol | 4.520 | 0.45 | 0.33 | 0.41 | 0.0 | C |
| 61 | Cyclopentanol | 3.270 | 0.40 | 0.32 | 0.48 | 0.0 | B,C |
| 62 | Cyclohexanol | 3.594 | 0.45 | 0.32 | 0.51 | 0.0 | C |
| 63 | Ethanethiol | 2.172 | 0.35 | 0.00 | 0.16 | 0.0 | C |
| 64 | *n*-Propanethiol | 2.685 | 0.35 | 0.00 | 0.16 | 0.0 | C |
| 65 | Isopropanethiol | 2.406 | 0.35 | 0.00 | 0.16 | 0.0 | C |
| 66 | Isobutanethiol | 2.880 | 0.35 | 0.00 | 0.16 | 0.0 | C |
| 67 | *n*-Butanethiol | 3.243 | 0.35 | 0.00 | 0.16 | 0.0 | C |
| 68 | *n*-Pentanethiol | 3.720 | 0.35 | 0.00 | 0.16 | 0.0 | C |
| 69 | Isopentanethiol | 3.360 | 0.35 | 0.00 | 0.16 | 0.0 | C |
| 70 | *n*-Hexanethiol | 4.220 | 0.35 | 0.00 | 0.16 | 0.0 | C |
| 71 | *n*-Heptanethiol | 4.720 | 0.35 | 0.00 | 0.16 | 0.0 | C |
| 72 | *n*-Octanethiol | 5.310 | 0.35 | 0.00 | 0.16 | 0.0 | C |
| 73 | *n*-Nonanethiol | 5.890 | 0.35 | 0.00 | 0.16 | 0.0 | C |
| 74 | *n*-Decanethiol | 6.480 | 0.35 | 0.00 | 0.16 | 0.0 | C |
| 75 | *tert.*-Butanethiol | 2.558 | 0.35 | 0.00 | 0.16 | 0.0 | C |
| 76 | Acetone | 1.760 | 0.71 | 0.04 | 0.50 | 0.0 | A,B,C |
| 77 | 2-Butanone | 2.287 | 0.67 | 0.00 | 0.48 | 0.0 | A,B,C |
| 78 | 2-Pentanone | 2.755 | 0.65 | 0.00 | 0.48 | 0.0 | A,B,C |
| 79 | 3-Hexanone | 3.310 | 0.65 | 0.00 | 0.48 | 0.0 | C |
| 80 | 2-Hexanone | 3.262 | 0.65 | 0.00 | 0.48 | 0.0 | C |
| 81 | 2-Heptanone | 3.760 | 0.65 | 0.00 | 0.48 | 0.0 | C |
| 82 | 2-Octanone | 4.257 | 0.65 | 0.00 | 0.48 | 0.0 | C |
| 83 | 2-Nonanone | 4.755 | 0.65 | 0.00 | 0.48 | 0.0 | C |
| 84 | 2-Decanone | 5.260 | 0.65 | 0.00 | 0.48 | 0.0 | C |
| 85 | 2-Undecanone | 5.760 | 0.65 | 0.00 | 0.48 | 0.0 | C |
| 86 | 2-Dodecanone | 6.260 | 0.65 | 0.00 | 0.48 | 0.0 | C |
| 87 | Carvone | 5.330 | 0.80 | 0.00 | 0.49 | 0.0 | C |
| 88 | Cyclopentanone | 3.120 | 0.76 | 0.00 | 0.52 | 0.0 | B,C |
| 89 | Cyclohexanone | 3.616 | 0.76 | 0.00 | 0.52 | 0.0 | B,C |
| 90 | Cycloheptanone | 4.110 | 0.76 | 0.00 | 0.52 | 0.0 | C |
| 91 | Cyclooctanone | 4.610 | 0.76 | 0.00 | 0.52 | 0.0 | C |
| 92 | Cyclononanone | 5.110 | 0.76 | 0.00 | 0.52 | 0.0 | C |
| 93 | Cyclodecanone | 5.610 | 0.76 | 0.00 | 0.52 | 0.0 | C |
| 94 | Cycloundecanone | 6.110 | 0.76 | 0.00 | 0.52 | 0.0 | C |
| 95 | Cyclododecanone | 6.600 | 0.76 | 0.00 | 0.52 | 0.0 | C |
| 96 | Acetonitrile | 1.560 | 0.75 | 0.09 | 0.44 | 0.0 | A,B,C |
| 97 | Propionitrile | 1.978 | 0.63 | 0.00 | 0.43 | 0.0 | A,B |
| 98 | 1-Cyanopropane | 2.540 | 0.68 | 0.00 | 0.44 | 0.0 | C |
| 99 | 1-Cyanobutane | 3.057 | 0.68 | 0.00 | 0.44 | 0.0 | C |
| 100 | Bromoethane | 2.120 | 0.48 | 0.00 | 0.17 | 0.0 | C |
| 101 | Iodomethane | 2.106 | 0.40 | 0.00 | 0.18 | 0.0 | C |
| 102 | Chlorobutane | 2.716 | 0.37 | 0.00 | 0.10 | 0.5 | B |
| 103 | 1-Iodobutane | 3.628 | 0.50 | 0.00 | 0.18 | 0.0 | C |
| 104 | 2-Iodobutane | 3.390 | 0.50 | 0.00 | 0.18 | 0.0 | C |

TABLE I *(continued)*

| No. | Compound | $\log L^{16a}$ | $\pi_2^{*b}$ | $\alpha_2^{Hc}$ | $\beta_2^{Hd}$ | $\delta_2{}^e$ | Ref.$^f$ |
|-----|----------|----------------|--------------|-----------------|----------------|----------------|----------|
| 105 | 1-Bromopentane | 3.611 | 0.48 | 0.00 | 0.17 | 0.0 | C |
| 106 | 1-Chlorohexane | 3.710 | 0.39 | 0.00 | 0.15 | 0.0 | C |
| 107 | 2-Bromooctane | 5.110 | 0.48 | 0.00 | 0.17 | 0.0 | C |
| 108 | Dichloromethane | 1.997 | 0.82 | 0.13 | 0.06 | 0.5 | B |
| 109 | 1,2-Dichloroethane | 2.573 | 0.81 | 0.10 | 0.05 | 0.5 | B,C |
| 110 | 1,1,2-Trichloroethane | 2.997 | 0.53 | 0.12 | 0.03 | 0.5 | C |
| 111 | Trichloromethane | 2.480 | 0.58 | 0.20 | 0.02 | 0.5 | B,C |
| 112 | Tetrachloromethane | 2.823 | 0.28 | 0.00 | 0.00 | 0.5 | A,B,C |
| 113 | Dimethyl sulfide | 2.238 | 0.36 | 0.00 | 0.29 | 0.0 | C |
| 114 | Diethyl sulfide | 3.104 | 0.36 | 0.00 | 0.29 | 0.0 | C |
| 115 | Di-*n*-propyl sulfide | 4.120 | 0.36 | 0.00 | 0.29 | 0.0 | C |
| 116 | Methyl-*n*-propyl sulfide | 3.240 | 0.36 | 0.00 | 0.29 | 0.0 | C |
| 117 | Isoamyl sulfide | 5.540 | 0.36 | 0.00 | 0.29 | 0.0 | C |
| 118 | Di-*n*-butyl sulfide | 4.950 | 0.36 | 0.00 | 0.29 | 0.0 | C |
| 119 | Diethyl disulfide | 4.210 | 0.64 | 0.00 | 0.22 | 0.0 | C |
| 120 | Acetic acid | 1.750 | 0.64 | 0.55 | 0.43 | 0.0 | A,B,C |
| 121 | *n*-Propanoic acid | 2.290 | 0.64 | 0.54 | 0.43 | 0.0 | B,C |
| 122 | *n*-Butanoic acid | 2.830 | 0.64 | 0.54 | 0.42 | 0.0 | B,C |
| 123 | 3-Methylbutanoic acid | 3.300 | 0.64 | 0.54 | 0.41 | 0.0 | C |
| 124 | *n*-Pentanoic acid | 3.380 | 0.64 | 0.54 | 0.41 | 0.0 | C |
| 125 | *n*-Hexanoic acid | 3.920 | 0.64 | 0.54 | 0.39 | 0.0 | C |
| 126 | *n*-Heptanoic acid | 4.460 | 0.64 | 0.54 | 0.38 | 0.0 | C |
| 127 | *n*-Octanoic acid | 5.000 | 0.64 | 0.54 | 0.36 | 0.0 | C |
| 128 | *n*-Nonanoic acid | 5.550 | 0.64 | 0.54 | 0.34 | 0.0 | C |
| 129 | *n*-Propyl formate | 2.413 | 0.61 | 0.00 | 0.38 | 0.0 | C |
| 130 | Methyl acetate | 1.960 | 0.64 | 0.00 | 0.40 | 0.0 | B,C |
| 131 | Ethyl acetate | 2.376 | 0.55 | 0.00 | 0.45 | 0.0 | A,B,C |
| 132 | *n*-Propyl acetate | 2.878 | 0.55 | 0.00 | 0.45 | 0.0 | A,B,C |
| 133 | *n*-Butyl acetate | 3.379 | 0.55 | 0.00 | 0.45 | 0.0 | C |
| 134 | *n*-Pentyl acetate | 3.810 | 0.55 | 0.00 | 0.45 | 0.0 | C |
| 135 | Isoamyl acetate | 3.740 | 0.55 | 0.00 | 0.45 | 0.0 | C |
| 136 | Methyl propanoate | 2.459 | 0.55 | 0.00 | 0.45 | 0.0 | C |
| 137 | Propyl butanoate | 3.810 | 0.55 | 0.00 | 0.45 | 0.0 | C |
| 138 | Isobutyl isobutanoate | 3.880 | 0.55 | 0.00 | 0.45 | 0.0 | C |
| 139 | Isoamyl isopentanoate | 4.580 | 0.55 | 0.00 | 0.45 | 0.0 | C |
| 140 | Acetaldehyde | 1.230 | 0.67 | 0.00 | 0.40 | 0.0 | C |
| 141 | Propionaldehyde | 1.815 | 0.65 | 0.00 | 0.40 | 0.0 | A,B,C |
| 142 | Butyraldehyde | 2.270 | 0.65 | 0.00 | 0.40 | 0.0 | C |
| 143 | Isobutyraldehyde | 2.060 | 0.65 | 0.00 | 0.40 | 0.0 | C |
| 144 | 3-Methylbutanal | 2.620 | 0.65 | 0.00 | 0.40 | 0.0 | C |
| 145 | Hexanal | 3.370 | 0.65 | 0.00 | 0.40 | 0.0 | C |
| 146 | Heptanal | 3.860 | 0.65 | 0.00 | 0.40 | 0.0 | C |
| 147 | Octanal | 4.380 | 0.65 | 0.00 | 0.40 | 0.0 | C |
| 148 | Propenal, acrolein | 2.110 | 0.65 | 0.00 | 0.40 | 0.0 | C |
| 149 | *trans*-But-2-en-1-al | 2.570 | 0.75 | 0.00 | 0.40 | 0.0 | C |
| 150 | Benzene | 2.803 | 0.59 | 0.00 | 0.14 | 1.0 | A,B,C |
| 151 | Toluene | 3.344 | 0.55 | 0.00 | 0.14 | 1.0 | A,B,C |
| 152 | Ethylbenzene | 3.765 | 0.53 | 0.00 | 0.15 | 1.0 | A,B,C |
| 153 | 2-Xylene | 3.937 | 0.51 | 0.00 | 0.17 | 1.0 | B,C |
| 154 | 3-Xylene | 3.864 | 0.51 | 0.00 | 0.17 | 1.0 | B,C |
| 155 | 4-Xylene | 3.858 | 0.51 | 0.00 | 0.17 | 1.0 | A,B,C |
| 156 | Propylbenzene | 4.239 | 0.51 | 0.00 | 0.12 | 1.0 | A,B |

TABLE I *(continued)*

| No. | Compound | $\log L^{16a}$ | $\pi_2^{*b}$ | $\alpha_2^{Hc}$ | $\beta_2^{Hd}$ | $\delta_2^{e}$ | Ref.$^f$ |
|-----|----------|------|------|------|------|------|------|
| 157 | Butylbenzene | 4.714 | 0.49 | 0.00 | 0.12 | 1.0 | B |
| 158 | Styrene | 3.908 | 0.55 | 0.00 | 0.18 | 1.0 | C |
| 159 | Mesitylene | 4.399 | 0.47 | 0.00 | 0.20 | 1.0 | C |
| 160 | Fluorobenzene | 2.785 | 0.62 | 0.00 | 0.07 | 1.0 | B |
| 161 | Chlorobenzene | 3.630 | 0.71 | 0.00 | 0.07 | 1.0 | B |
| 162 | Bromobenzene | 4.022 | 0.79 | 0.00 | 0.06 | 1.0 | B |
| 163 | Iodobenzene | 4.505 | 0.81 | 0.00 | 0.05 | 1.0 | B |
| 164 | 1,2-Dichlorobenzene | 4.405 | 0.80 | 0.00 | 0.03 | 1.0 | B,C |
| 165 | *p*-Dichlorobenzene | 4.404 | 0.70 | 0.00 | 0.03 | 1.0 | B |
| 166 | Diethylether | 2.061 | 0.27 | 0.00 | 0.45 | 0.0 | A,B,C |
| 167 | Dipropylether | 2.971 | 0.27 | 0.00 | 0.46 | 0.0 | A,B |
| 168 | Di(isopropyl) ether | 2.561 | 0.27 | 0.00 | 0.47 | 0.0 | B |
| 169 | Di-*n*-butyl ether | 4.001 | 0.27 | 0.00 | 0.45 | 0.0 | A,B,C |
| 170 | Dioxane | 2.788 | 0.55 | 0.00 | 0.47 | 0.0 | B |
| 171 | Nitromethane | 1.892 | 0.85 | 0.12 | 0.25 | 0.0 | A,B,C |
| 172 | Nitroethane | 2.367 | 0.80 | 0.00 | 0.25 | 0.0 | A,B,C |
| 173 | 1-Nitropropane | 2.850 | 0.79 | 0.00 | 0.25 | 0.0 | A,B,C |
| 174 | Thiophene | 2.943 | 0.60 | 0.00 | 0.16 | 1.0 | C |
| 175 | 2-Methylthiophene | 3.302 | 0.40 | 0.0 | 0.14 | 1.0 | C |
| 176 | 2,5-Dimethylthiophene | 3.806 | 0.40 | 0.00 | 0.16 | 1.0 | C |
| 177 | Nitrobenzene | 4.433 | 1.01 | 0.00 | 0.30 | 1.0 | B |
| 178 | Benzyl chloride | 4.290 | 0.71 | 0.00 | 0.31 | 1.0 | C |
| 179 | 3-Nitrotoluene | 4.970 | 0.97 | 0.00 | 0.34 | 1.0 | C |
| 180 | Furan | 1.830 | 0.50 | 0.00 | 0.15 | 1.0 | C |
| 181 | Allyl mercaptan | 2.510 | 0.40 | 0.00 | 0.20 | 0.0 | C |
| 182 | Tetrahydrofuran | 2.521 | 0.58 | 0.00 | 0.51 | 0.0 | A,B |
| 183 | Phenylethyne | 3.715 | 0.55 | 0.12 | 0.21 | 1.0 | C |
| 184 | Anisole | 3.916 | 0.73 | 0.00 | 0.26 | 1.0 | B,C |
| 185 | Pyridine | 3.003 | 0.87 | 0.00 | 0.62 | 1.0 | B,C |
| 186 | Benzonitrile | 4.004 | 0.90 | 0.00 | 0.42 | 1.0 | A,B |
| 187 | Benzaldehyde | 3.985 | 0.92 | 0.00 | 0.42 | 1.0 | A,B |
| 188 | Acetophenone | 4.483 | 0.90 | 0.00 | 0.51 | 1.0 | B,C |
| 189 | N,N-Dimethylaniline | 4.753 | 0.90 | 0.00 | 0.35 | 1.0 | A,B |
| 190 | Phenol | 3.641 | 0.72 | 0.60 | 0.22 | 1.0 | A,B |
| 191 | Aniline | 3.934 | 0.73 | 0.26 | 0.38 | 1.0 | A,B |
| 192 | *m*-Cresol | 4.329 | 0.68 | 0.58 | 0.24 | 1.0 | A |
| 193 | Benzyl alcohol | 4.162 | 0.99 | 0.39 | 0.42 | 1.0 | A,B |
| 194 | N-methylaniline | 4.492 | 0.73 | 0.17 | 0.47 | 1.0 | A,B |
| 195 | Triethylamine | 3.008 | 0.14 | 0.00 | 0.67 | 0.0 | A,B |
| 196 | Dimethylsulfoxide | 3.110 | 1.00 | 0.00 | 0.78 | 0.0 | A,B |
| 197 | Dimethylacetamide | 3.357 | 0.88 | 0.00 | 0.74 | 0.0 | A,B |
| 198 | Dimethylformamide | 2.922 | 0.88 | 0.00 | 0.66 | 0.0 | A,B |
| 199 | Trifluoroethanol | 1.315 | 0.73 | 0.57 | 0.18 | 0.0 | A,B |
| 200 | Hexanfluoroisopropanol | 1.370 | 0.65 | 0.77 | 0.03 | 0.0 | A,B |
| 201 | Ethylamine | 1.677 | 0.32 | 0.00 | 0.70 | 0.0 | A,B |
| 202 | Propylamine | 2.141 | 0.31 | 0.00 | 0.69 | 0.0 | A |
| 203 | Butylamine | 2.618 | 0.31 | 0.00 | 0.69 | 0.0 | A |

$^a$ From refs. 37 and 38.
$^b$ From refs. 37 and 24.
$^c$ From refs. 37 and 39.
$^d$ From refs. 37 and 40.
$^e$ From refs. 25 and 37.
$^f$ Data base, see text.

RESULTS

Mutual correlation results for the different types of columns used in this work are given in Tables II and III. It is evident that quite a few of the columns are very strongly correlated. This results because they are both very non-polar and have low basicity. As expected, there are also strong correlations between the basic phases (*e.g.*, TEHP, DEDA, BPP). However, it is clear that a number of the phases are very weakly correlated. Such phases must be included in the data base to insure a numerically stable computation. Some thought indicates that the various phases can behave independently only when the common solute set, that is, those solutes which were run on all of the columns, explore a diverse set of chemical interactions. Thus, for example, if only non-polar solutes were run, all of the columns would appear to be strongly correlated.

The initial, conventional least squares regressions using the initial set of parameters given in Table I (from Abraham) gave fairly poor fits (see Table IV). The standard deviations of the fits ranged from as low as 0.052 for the low polarity phases to as high as 0.182 for the more polar and basic phases. The corresponding correlation coefficients ranged from 0.998 to 0.971. If the lack of fit were due to random experimental errors in the measured $k'$ values then it should not be possible to systematically improve the fit on all of the columns by using a new set of adjusted parameters, however, the standard deviations of the fit are very much improved when the new parameters were used (see Table IV) indicating that the lack of fit is not random and not due to experimental errors in the $k'$ values.

There are two distinct ways in which adjusting the parameters could improve the fit. First the initial parameter set could contain significant determinate errors which were corrected by the fitting procedures. Second, the fundamental model, that is the LSER, could be invalid or incomplete and adjusting the parameters compensated for the deficiencies in the model. We are aware of several shortcomings of the above LSER. The most serious are that it combines the dispersive interactions [19] and cavity formation processes [42,43] into a single parameter (log $L^{16}$) and a single fitting coefficient $l$; further it ignores the existence of differences in configurational entropies and free volume effects [44,45] between the various types of phases which span a very wide range in molecular weights. We also note that it may well be, as discussed above, that a solute can interact with its environment so strongly that its *relative* hydrogen bonding strength is perturbed [40].

The accuracy and indeed the validity of our entire methodology is based on the use of log $L^{16}$ as an explanatory variable. There are two possible difficulties with this idea. First, is the relatively trivial problem that individual values of log $L^{16}$ may be in error. This problem will propagate into an error in $\pi_2^{*,C}$ and then into an error in $\alpha_2^C$. Second, far more seriously, any error in log $L^{16}$ as a general model of the combined cavity and dispersive interaction, will complicate the interpretation of $\pi_2^{*,C}$. In order to examine this, we have done the same calculations based on retention data using a squalane column, log $L^{\text{squalane}}$ [46], as a substitute for log $L^{16}$. There were no appreciable differences in the results ($\pi_2^{*,C}$) obtained. It is very likely that log $L^{16}$ is as good, if not better, than any other single parameter used to model the gas–liquid partition process in non-polar solvents. We are still uncomfortable with the use of a single parameter that purports to represent both dispersive interaction and cavity formation processes (see below).

TABLE II

MUTAL CORRELATION BETWEEN THE PHASES (WITHIN DATA BASE A AND B) USED TO GENERATE THE NEW PARAMETERS

| Phase type | Correlation coefficients[a] | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | DB-1 | DB-5 | DB-1301 | DB-1701 | DB-17 | DB-210 | DB-225 | DB-WAX | TEHP | TOPO | MDOA | DMDA | BPP | DEDA |
| DB-1 | 1.000 | | | | | | | | | | | | | |
| DB-5 | 0.998 | 1.000 | | | | | | | | | | | | |
| DB-1301 | 0.971 | 0.976 | 1.000 | | | | | | | | | | | |
| DB-1701 | 0.930 | 0.941 | 0.989 | 1.000 | | | | | | | | | | |
| DB-17 | 0.941 | 0.957 | 0.979 | 0.986 | 1.000 | | | | | | | | | |
| DB-210 | 0.803 | 0.832 | 0.877 | 0.914 | 0.938 | 1.000 | | | | | | | | |
| DB-225 | 0.745 | 0.772 | 0.868 | 0.930 | 0.923 | 0.929 | 1.000 | | | | | | | |
| DB-WAX | 0.604 | 0.636 | 0.743 | 0.827 | 0.822 | 0.832 | 0.964 | 1.000 | | | | | | |
| TEHP | 0.567 | 0.566 | 0.741 | 0.808 | 0.840 | 0.531 | 0.800 | 0.877 | 1.000 | | | | | |
| TOPO | 0.619 | 0.632 | 0.709 | 0.765 | 0.762 | 0.632 | 0.809 | 0.870 | 0.936 | 1.000 | | | | |
| MDOA | 0.978 | 0.971 | 0.955 | 0.917 | 0.905 | 0.720 | 0.773 | 0.708 | 0.898 | 0.824 | 1.000 | | | |
| DMDA | 0.814 | 0.805 | 0.889 | 0.892 | 0.880 | 0.661 | 0.806 | 0.792 | 0.958 | 0.883 | 0.989 | 1.000 | | |
| BPP | 0.730 | 0.733 | 0.848 | 0.892 | 0.900 | 0.700 | 0.874 | 0.884 | 0.995 | 0.931 | 0.939 | 0.975 | 1.000 | |
| DEDA | 0.696 | 0.703 | 0.828 | 0.879 | 0.893 | 0.705 | 0.881 | 0.909 | 0.997 | 0.952 | 0.907 | 0.957 | 0.996 | 1.000 |

[a] For 48 compounds included in both A and B data bases.

TABLE III

MUTUAL CORRELATON BETWEEN THE PHASES (IN DATA BASE C) USED TO GENERATE THE NEW PARAMETERS

| Phase Type | Correlation coefficients[a] | | | | |
|---|---|---|---|---|---|
| | ZE7 | Carbowax | TCEP | PPE | DEGS |
| ZE7 | 1.000 | | | | |
| Carbowax | 0.947 | 1.000 | | | |
| TCEP | 0.932 | 0.970 | 1.000 | | |
| PPE6 | 0.962 | 0.920 | 0.861 | 1.000 | |
| DEGS | 0.943 | 0.987 | 0.993 | 0.895 | 1.000 |

[a] For all compounds ($n = 166$) in data base C.

It is well known [47] that non-polar compounds can adsorb at the gas–liquid surface of a polar stationary phase, and a polar compound will only weakly partition into a non-polar phase. How then can we use log $L^{16}$ to simultaneously model both non-polar and polar solutes in all the phases? That is, will the parameter values vary

TABLE IV

QUALITY OF THE INITIAL AND FINAL FITS

Eqn. 6 is the regression equation employed.

| Phase | Temperature | Initial | | Final | | $n^c$ |
|---|---|---|---|---|---|---|
| | | S.D.[a] | $r^b$ | S.D.[a] | $r^b$ | |
| DB-1 | 80 | 0.052 | 0.998 | 0.029 | 0.999 | 53 |
| DB-5 | 80 | 0.065 | 0.997 | 0.034 | 0.999 | 53 |
| DB-1301 | 80 | 0.103 | 0.992 | 0.046 | 0.998 | 52 |
| DB-1701 | 80 | 0.114 | 0.991 | 0.030 | 0.999 | 53 |
| DB-17 | 80 | 0.127 | 0.989 | 0.044 | 0.999 | 51 |
| DB-210 | 80 | 0.151 | 0.979 | 0.056 | 0.997 | 53 |
| DB-225 | 80 | 0.176 | 0.980 | 0.037 | 0.999 | 53 |
| DB-WAX | 115 | 0.182 | 0.971 | 0.040 | 0.999 | 74 |
| TEHP | 110 | 0.126 | 0.977 | 0.034 | 0.998 | 70 |
| TOPO | 100 | 0.159 | 0.984 | 0.058 | 0.998 | 83 |
| MDOA | 60 | 0.070 | 0.996 | 0.047 | 0.998 | 72 |
| DMDA | 50 | 0.150 | 0.984 | 0.053 | 0.998 | 75 |
| BPP | 60 | 0.151 | 0.986 | 0.033 | 0.999 | 77 |
| DEDA | 70 | 0.148 | 0.985 | 0.046 | 0.999 | 79 |
| ZE7 | 120 | 0.125 | 0.984 | 0.101 | 0.990 | 166 |
| Carbowax | 120 | 0.135 | 0.986 | 0.043 | 0.999 | 166 |
| TCEP | 120 | 0.162 | 0.982 | 0.042 | 0.999 | 166 |
| PPE6 | 120 | 0.112 | 0.990 | 0.050 | 0.998 | 166 |
| DEGS | 120 | 0.164 | 0.979 | 0.042 | 0.999 | 166 |

[a] Standard deviation of the fit.
[b] Correlation coefficient.
[c] Number of solutes included in the regression.

with the phase? We plotted the $\pi_2^{*,C}$ values of five very different but quite representative compounds (pentane, butylether, ethanol, 2-pentanone and nitropropane) on five very different stationary phases (DB-17, DB-225, BPP, TOPO, DEGS) (see Fig. 1). Clearly the parameters do not vary much from phase to phase. We need to point out that adsorption effects in our data set are not very important. We used several different phase loadings on the TOPO column and as expected we obtained the same coefficients $(l, s, a, b, d)$. The intercept $(XYZ_0)$, which does depend on the phase loadings, did vary.

The final sets of the chromatographically based $\pi_2^{*,C}$ and $\alpha_2^C$ parameters are given in Table V along with a measure of the uncertainty in the parameter. The uncertainty was obtained as the standard deviation in the parameter over all of the columns used to compute it. Typically, the standard deviation in $\pi_2^{*,C}$ is 0.01 to 0.02. Values for the highly acidic compounds can be as large as 0.10, but this is certainly extreme. The standard deviations in $\pi_2^{*,C}$ represent the column-to-column variations in the computed value of $\pi_2^{*,C}$. To give some idea of how good or how bad this is, we note that when $\pi^*$ is determined by the original solvatochromic methodology, developed by Kamlet *et al.* [6], the variation from indicator to indicator, in select solvents, is often 0.05. In hydrogen bond donor solvents, the variation in $\pi^*$ can be as large as 0.10. Thus on the whole we are pleased with the reliability of the $\pi_2^{*,C}$ values, although we do hope to improve the reliability of those solutes which are strong hydrogen bond donors.

Based on the computational procedure outlined above, the $\alpha_2^C$ values cannot be better defined than $\pi_2^{*,C}$ since $\alpha_2^C$ is computed based on the estimates of $\pi_2^{*,C}$. Thus any column-to-column variation in $\pi_2^{*,C}$ will be reflected in $\alpha_2^C$. In addition the experimental error in the additional $k'$ values on the columns used to compute $\alpha_2^C$ will show up in the reliability of $\alpha_2^C$. Nonetheless the standard deviation in $\alpha_2^C$ seem to be quite acceptable.

DISCUSSION

### $\pi_2^{*,C}$ *Values*

The fundamental issue is whether or not the procedure described above is merely an exercise in data fitting, that is, do the new parameters have any underlying
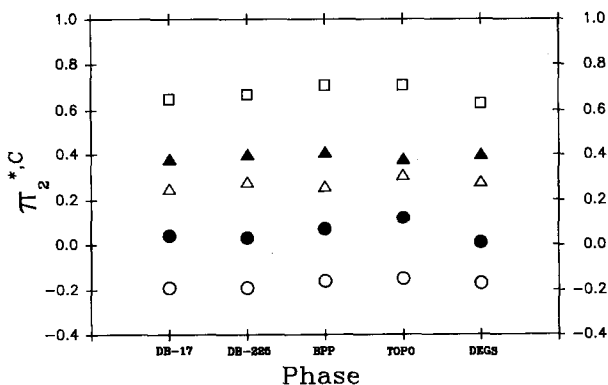


Fig. 1. $\pi_2^{*,C}$ *versus* GC phases used to compute it. $\bigcirc$ = Pentane; $\bullet$ = butyl ether; $\triangle$ = ethanol; $\blacktriangle$ = 2-pentanone and $\blacksquare$ = nitropropane.

TABLE V

FINAL SOLUTE DIPOLARITY/POLARIZABILITY AND HYDROGEN BOND ACIDITY PARAMETERS

| No. | Compound | $\pi_2^{*,Ca}$ | S.D.$^b$ | $n_1{}^c$ | $n_2{}^d$ | $\alpha_2^{Ca}$ | S.D.$^e$ | $n_3{}^f$ | $n_4{}^g$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Propane | −0.17 | 0.01 | 3 | 0 | 0.00 | | | |
| 2 | Isobutane | −0.17 | 0.01 | 3 | 0 | 0.00 | | | |
| 3 | Butane | −0.17 | 0.01 | 3 | 0 | 0.00 | | | |
| 4 | Pentane | −0.18 | 0.02 | 11 | 0 | 0.00 | | | |
| 5 | 2,4-Dimethylpentane | −0.18 | 0.05 | 3 | 0 | 0.00 | | | |
| 6 | 2-Methylpentane | −0.14 | 0.01 | 3 | 0 | 0.00 | | | |
| 7 | Hexane | −0.16 | 0.01 | 11 | 0 | 0.00 | | | |
| 8 | 2,2,5-Trimethylhexane | −0.16 | 0.02 | 3 | 0 | 0.00 | | | |
| 9 | $n$-Heptane | −0.14 | 0.01 | 7 | 0 | 0.00 | | | |
| 10 | 3-Methylheptane | −0.12 | 0.01 | 3 | 0 | 0.00 | | | |
| 11 | 2-Methylheptane | −0.13 | 0.01 | 3 | 0 | 0.00 | | | |
| 12 | $n$-Octane | −0.12 | 0.01 | 11 | 0 | 0.00 | | | |
| 13 | $n$-Nonane | −0.12 | 0.02 | 7 | 0 | 0.00 | | | |
| 14 | $n$-Decane | −0.11 | 0.01 | 11 | 0 | 0.00 | | | |
| 15 | $n$-Undecane | −0.10 | 0.01 | 11 | 0 | 0.00 | | | |
| 16 | $n$-Dodecane | −0.09 | 0.01 | 7 | 0 | 0.00 | | | |
| 17 | $n$-Tridecane | −0.08 | 0.02 | 7 | 0 | 0.00 | | | |
| 18 | $n$-Tetradecane | −0.07 | 0.01 | 9 | 1 | 0.00 | | | |
| 19 | $n$-Pentadecane | −0.06 | 0.01 | 4 | 0 | 0.00 | | | |
| 20 | Cyclopentane | −0.07 | 0.02 | 4 | 0 | 0.00 | | | |
| 21 | Cyclohexane | 0.00 | 0.03 | 11 | 0 | 0.00 | | | |
| 22 | Cycloheptane | 0.00 | 0.02 | 4 | 0 | 0.00 | | | |
| 23 | Propene | −0.00 | 0.05 | 3 | 0 | 0.00 | | | |
| 24 | 1-Butene | −0.02 | 0.04 | 3 | 0 | 0.00 | | | |
| 25 | 1-Pentene | −0.02 | 0.04 | 3 | 0 | 0.00 | | | |
| 26 | 1-Hexene | −0.07 | 0.02 | 10 | 0 | 0.00 | | | |
| 27 | 1-Heptene | −0.05 | 0.01 | 3 | 0 | 0.00 | | | |
| 28 | $cis$-2-Octene | −0.02 | 0.01 | 3 | 0 | 0.00 | | | |
| 29 | 2-Ethyl-1-hexene | −0.02 | 0 | 3 | 0 | 0.00 | | | |
| 30 | 1-Octene | −0.05 | 0.01 | 3 | 0 | 0.00 | | | |
| 31 | $\alpha$-Pinene | 0.07 | 0.02 | 3 | 0 | 0.00 | | | |
| 32 | 1-Octyne | 0.16 | 0.01 | 3 | 0 | 0.04 | 0.02 | 3 | 0 |
| 33 | 2-Octyne | 0.23 | 0.03 | 3 | 0 | 0.00 | | | |
| 34 | Methanol | 0.35 | 0.05 | 11 | 1 | 0.35 | 0.04 | 11 | 1 |
| 35 | Ethanol | 0.29 | 0.03 | 11 | 0 | 0.29 | 0.03 | 11 | 1 |
| 36 | 1-Propanol | 0.30 | 0.02 | 11 | 0 | 0.32 | 0.03 | 12 | 0 |
| 37 | 1-Butanol | 0.30 | 0.02 | 4 | 0 | 0.31 | 0.01 | 7 | 0 |
| 38 | 2-Methyl-1-propanol | 0.30 | 0.03 | 6 | 0 | 0.31 | 0.01 | 9 | 0 |
| 39 | 2-Methyl-1-butanol | 0.27 | 0.01 | 3 | 0 | 0.35 | 0.02 | 3 | 0 |
| 40 | Isopentanol | 0.28 | 0.01 | 4 | 0 | 0.34 | 0.01 | 7 | 0 |
| 41 | 1-Pentanol | 0.32 | 0.01 | 7 | 0 | 0.32 | 0.01 | 10 | 0 |
| 42 | 1-Hexanol | 0.33 | 0.01 | 6 | 0 | 0.34 | 0.01 | 10 | 0 |
| 43 | 1-Heptanol | 0.35 | 0.01 | 5 | 0 | 0.33 | 0.01 | 7 | 0 |
| 44 | 1-Octanol | 0.36 | 0.01 | 3 | 0 | 0.35 | 0.02 | 3 | 0 |
| 45 | 1-Nonanol | 0.38 | 0.01 | 3 | 0 | 0.34 | 0.01 | 3 | 0 |
| 46 | 1-Decanol | 0.40 | 0 | 3 | 0 | 0.32 | 0.01 | 3 | 0 |
| 47 | 1-Undecanol | 0.43 | 0 | 3 | 0 | 0.33 | 0.01 | 3 | 0 |
| 48 | 1-Dodecanol | 0.45 | 0.01 | 3 | 0 | 0.34 | 0.02 | 3 | 0 |
| 49 | 2-Propanol | 0.21 | 0.02 | 9 | 0 | 0.29 | 0.03 | 10 | 0 |
| 50 | 2-Butanol | 0.24 | 0.02 | 6 | 0 | 0.28 | 0.02 | 9 | 0 |
| 51 | 2-Hexanol | 0.27 | 0 | 3 | 0 | 0.28 | 0.01 | 3 | 0 |

ABLE V *(continued)*

| o. | Compound | $\pi_2^{*,Ca}$ | S.D.[b] | $n_1{}^c$ | $n_2{}^d$ | $\alpha_2^{Ca}$ | S.D.[e] | $n_3{}^f$ | $n_4{}^g$ |
|---|---|---|---|---|---|---|---|---|---|
| i2 | 3-Hexanol | 0.21 | 0.02 | 3 | 0 | 0.30 | 0.02 | 3 | 0 |
| i3 | *tert.*-Butanol | 0.19 | 0.03 | 11 | 0 | 0.25 | 0.04 | 12 | 1 |
| i4 | 3-Methyl-3-pentanol | 0.19 | 0.02 | 3 | 0 | 0.27 | 0.03 | 3 | 0 |
| i5 | 2-Methyl-2-pentanol | 0.16 | 0.02 | 3 | 0 | 0.29 | 0.03 | 3 | 0 |
| i6 | 2-Methyl-2-heptanol | 0.25 | 0 | 3 | 0 | 0.24 | 0.01 | 3 | 0 |
| i7 | Prop-2-en-1-ol | 0.33 | 0.02 | 3 | 0 | 0.38 | 0.03 | 3 | 0 |
| i8 | 2-Hexenol | 0.41 | 0.01 | 3 | 0 | 0.32 | 0.01 | 3 | 0 |
| i9 | *trans*-2-Heptenol | 0.45 | 0.02 | 3 | 0 | 0.31 | 0.02 | 3 | 0 |
| i0 | *trans*-2-Octenol | 0.45 | 0.01 | 3 | 0 | 0.33 | 0.02 | 3 | 0 |
| i1 | Cyclopentanol | 0.40 | 0 | 3 | 0 | 0.28 | 0.01 | 3 | 0 |
| i2 | Cyclohexanol | 0.37 | 0.04 | 4 | 0 | 0.31 | 0.03 | 7 | 0 |
| i4 | Ethanethiol | 0.17 | 0.01 | 3 | 0 | 0.00 | | | |
| i4 | *n*-Propanethiol | 0.19 | 0.01 | 3 | 0 | 0.00 | | | |
| i5 | Isopropanethiol | 0.15 | 0.01 | 3 | 0 | 0.00 | | | |
| i6 | Isobutanethiol | 0.20 | 0.01 | 3 | 0 | 0.00 | | | |
| i7 | *n*-Butanethiol | 0.20 | 0.02 | 3 | 0 | 0.00 | | | |
| i8 | *n*-Pentanethiol | 0.22 | 0.01 | 3 | 0 | 0.00 | | | |
| i9 | Isopentanethiol | 0.22 | 0.02 | 3 | 0 | 0.00 | | | |
| 70 | *n*-Hexanethiol | 0.24 | 0.01 | 3 | 0 | 0.00 | | | |
| 71 | *n*-Heptanethiol | 0.25 | 0.01 | 3 | 0 | 0.00 | | | |
| 72 | *n*-Octanethiol | 0.26 | 0.01 | 3 | 0 | 0.00 | | | |
| 73 | *n*-Nonanethiol | 0.26 | 0.02 | 3 | 0 | 0.00 | | | |
| 74 | *n*-Decanethiol | 0.26 | 0.02 | 3 | 0 | 0.00 | | | |
| 75 | *tert.*-Butanethiol | 0.11 | 0 | 3 | 0 | 0.00 | | | |
| 76 | Acetone | 0.38 | 0.03 | 11 | 1 | 0.01 | 0.01 | 12 | 0 |
| 77 | 2-Butanone | 0.39 | 0.02 | 11 | 1 | 0.00 | | | |
| 78 | 2-Pentanone | 0.40 | 0.02 | 11 | 1 | 0.00 | | | |
| 79 | 3-Hexanone | 0.34 | 0.01 | 3 | 0 | 0.00 | | | |
| 80 | 2-Hexanone | 0.39 | 0.02 | 3 | 0 | 0.00 | | | |
| 81 | 2-Heptanone | 0.41 | 0.01 | 3 | 0 | 0.00 | | | |
| 82 | 2-Octanone | 0.43 | 0.01 | 3 | 0 | 0.00 | | | |
| 83 | 2-Nonanone | 0.44 | 0.01 | 3 | 0 | 0.00 | | | |
| 84 | 2-Decanone | 0.45 | 0.01 | 3 | 0 | 0.00 | | | |
| 85 | 2-Undecanone | 0.45 | 0.01 | 3 | 0 | 0.00 | | | |
| 86 | 2-Dodecanone | 0.46 | 0.01 | 3 | 0 | 0.00 | | | |
| 87 | Carvone | 0.70 | 0.06 | 3 | 0 | 0.00 | | | |
| 88 | Cyclopentanone | 0.58 | 0.03 | 7 | 0 | 0.00 | | | |
| 89 | Cyclohexanone | 0.59 | 0.03 | 7 | 0 | 0.00 | | | |
| 90 | Cycloheptanone | 0.66 | 0.01 | 3 | 0 | 0.00 | | | |
| 91 | Cyclooctanone | 0.69 | 0.02 | 3 | 0 | 0.00 | | | |
| 92 | Cyclononanone | 0.72 | 0.02 | 3 | 0 | 0.00 | | | |
| 93 | Cyclodecanone | 0.75 | 0.03 | 3 | 0 | 0.00 | | | |
| 94 | Cycloundecanone | 0.78 | 0.04 | 3 | 0 | 0.00 | | | |
| 95 | Cyclododecanone | 0.81 | 0.04 | 3 | 0 | 0.00 | | | |
| 96 | Acetonitrile | 0.62 | 0.03 | 11 | 0 | 0.05 | 0.02 | 12 | 0 |
| 97 | Propionitrile | 0.64 | 0.03 | 8 | 0 | 0.00 | | | |
| 98 | 1-Cyanopropane | 0.57 | 0.02 | 3 | 0 | 0.00 | | | |
| 99 | 1-Cyanobutane | 0.57 | 0.02 | 3 | 0 | 0.00 | | | |
| 00 | Bromoethane | 0.22 | 0 | 3 | 0 | 0.00 | | | |
| 01 | Iodomethane | 0.27 | 0.02 | 3 | 0 | 0.00 | | | |
| 02 | Chlorobutane | 0.21 | 0.01 | 3 | 0 | 0.00 | | | |
| 03 | 1-Iodobutane | 0.27 | 0 | 3 | 0 | 0.00 | | | |
| 04 | 2-Iodobutane | 0.26 | 0 | 3 | 0 | 0.00 | | | |

TABLE V *(continued)*

| No. | Compound | $\pi_2^{*,Ca}$ | S.D.[b] | $n_1{}^c$ | $n_2{}^d$ | $\alpha_2^{Ca}$ | S.D.[e] | $n_3{}^f$ | $n_4{}^g$ |
|---|---|---|---|---|---|---|---|---|---|
| 105 | 1-Bromopentane | 0.24 | 0 | 3 | 0 | 0.00 | | | |
| 106 | 1-Chlorohexane | 0.20 | 0.01 | 3 | 0 | 0.00 | | | |
| 107 | 2-Bromooctane | 0.21 | 0.01 | 3 | 0 | 0.00 | | | |
| 108 | Dichloromethane | 0.34 | 0.04 | 4 | 0 | 0.06 | 0.02 | 7 | 0 |
| 109 | 1,2-Dichloroethane | 0.39 | 0.03 | 5 | 0 | 0.05 | 0.04 | 8 | 0 |
| 110 | 1,1,2-Trichloroethane | 0.27 | 0.01 | 3 | 0 | 0.00 | | | |
| 111 | Trichloromethane | 0.27 | 0.05 | 6 | 0 | 0.16 | 0.02 | 10 | 0 |
| 112 | Tetrachloromethane | 0.16 | 0.03 | 11 | 0 | 0.00 | | | |
| 113 | Dimethyl sulfide | 0.18 | 0 | 3 | 0 | 0.00 | | | |
| 114 | Diethyl sulfide | 0.18 | 0.01 | 3 | 0 | 0.00 | | | |
| 115 | Di-*n*-propyl sulfide | 0.18 | 0.01 | 3 | 0 | 0.00 | | | |
| 116 | Methyl-*n*-propyl sulfide | 0.18 | 0.01 | 3 | 0 | 0.00 | | | |
| 117 | Isoamyl sulfide | 0.19 | 0.02 | 3 | 0 | 0.00 | | | |
| 118 | Di-*n*-butyl sulfide | 0.22 | 0.02 | 3 | 0 | 0.00 | | | |
| 119 | Diethyl disulfide | 0.36 | 0.01 | 3 | 0 | 0.00 | | | |
| 120 | Acetic acid | 0.50 | 0.05 | 10 | 0 | 0.72 | 0.06 | 10 | 0 |
| 121 | *n*-Propanoic acid | 0.61 | 0.02 | 3 | 0 | 0.67 | 0.06 | 7 | 0 |
| 122 | *n*-Butanoic acid | 0.57 | 0.02 | 3 | 0 | 0.62 | 0.04 | 7 | 0 |
| 123 | 3-Methylbutanoic acid | 0.45 | 0.04 | 3 | 0 | 0.69 | 0.04 | 3 | 0 |
| 124 | *n*-Pentanoic acid | 0.56 | 0.02 | 3 | 0 | 0.62 | 0.03 | 3 | 0 |
| 125 | *n*-Hexanoic acid | 0.60 | 0.05 | 3 | 0 | 0.52 | 0.06 | 3 | 0 |
| 126 | *n*-Heptanoic acid | 0.64 | 0.06 | 3 | 0 | 0.47 | 0.08 | 3 | 0 |
| 127 | *n*-Octanoic acid | 0.68 | 0.08 | 3 | 0 | 0.41 | 0.1 | 3 | 0 |
| 128 | *n*-Nonanoic acid | 0.72 | 0.1 | 3 | 0 | 0.35 | 0.12 | 3 | 0 |
| 129 | *n*-Propyl formate | 0.34 | 0 | 3 | 0 | 0.00 | | | |
| 130 | Methyl acetate | 0.30 | 0.05 | 7 | 0 | 0.00 | | | |
| 131 | Ethyl acetate | 0.30 | 0.04 | 11 | 0 | 0.00 | | | |
| 132 | *n*-Propyl acetate | 0.31 | 0.04 | 11 | 0 | 0.00 | | | |
| 133 | *n*-Butyl acetate | 0.33 | 0.01 | 3 | 0 | 0.00 | | | |
| 134 | *n*-Pentyl acetate | 0.35 | 0.02 | 3 | 0 | 0.00 | | | |
| 135 | Isoamyl acetate | 0.30 | 0.01 | 3 | 0 | 0.00 | | | |
| 136 | Methyl propanoate | 0.32 | 0.01 | 3 | 0 | 0.00 | | | |
| 137 | *n*-Propyl butanoate | 0.29 | 0.01 | 3 | 0 | 0.00 | | | |
| 138 | Isobutyl isobutanoate | 0.23 | 0.02 | 3 | 0 | 0.00 | | | |
| 139 | Isoamyl isopentanoate | 0.32 | 0.03 | 3 | 0 | 0.00 | | | |
| 140 | Acetaldehyde | 0.36 | 0.01 | 3 | 0 | 0.00 | | | |
| 141 | Propionaldehyde | 0.35 | 0:01 | 11 | 0 | 0.00 | | | |
| 142 | Butyraldehyde | 0.34 | 0.01 | 3 | 0 | 0.00 | | | |
| 143 | Isobutyralodehyde | 0.30 | 0.01 | 3 | 0 | 0.00 | | | |
| 144 | 3-Methylbutanal | 0.31 | 0.02 | 3 | 0 | 0.00 | | | |
| 145 | Hexanal | 0.36 | 0.01 | 3 | 0 | 0.00 | | | |
| 146 | Heptanal | 0.38 | 0.01 | 3 | 0 | 0.00 | | | |
| 147 | Octanal | 0.38 | 0.01 | 3 | 0 | 0.00 | | | |
| 148 | Propenal, acrolein | 0.34 | 0.01 | 3 | 0 | 0.00 | | | |
| 149 | *trans*-But-2-en-1-al | 0.50 | 0.01 | 3 | 0 | 0.00 | | | |
| 150 | Benzene | 0.29 | 0.01 | 11 | 0 | 0.00 | | | |
| 151 | Toluene | 0.29 | 0.02 | 11 | 0 | 0.00 | | | |
| 152 | Ethylbenzene | 0.30 | 0.02 | 11 | 0 | 0.00 | | | |
| 153 | 2-Xylene | 0.31 | 0.02 | 7 | 0 | 0.00 | | | |
| 154 | 3-Xylene | 0.29 | 0.02 | 6 | 0 | 0.00 | | | |
| 155 | 4-Xylene | 0.28 | 0.02 | 11 | 0 | 0.00 | | | |
| 156 | Propylbenzene | 0.30 | 0.02 | 8 | 0 | 0.00 | | | |

BLE V *(continued)*

| Compound | $\pi_2^{*,Ca}$ | S.D.$^b$ | $n_1{}^c$ | $n_2{}^d$ | $\alpha_2^{Ca}$ | S.D.$^e$ | $n_3{}^f$ | $n_4{}^g$ |
|---|---|---|---|---|---|---|---|---|
| Butylbenzene | 0.30 | 0.03 | 4 | 0 | 0.00 | | | |
| Styrene | 0.42 | 0.02 | 3 | 0 | 0.00 | | | |
| Mesitylene | 0.33 | 0 | 3 | 0 | 0.00 | | | |
| Fluorobenzene | 0.36 | | | | 0.00 | | | |
| Chlorobenzene | 0.42 | 0.01 | 4 | 0 | 0.00 | | | |
| Bromobenzene | 0.48 | 0.02 | 4 | 0 | 0.00 | | | |
| Iodobenzene | 0.55 | 0.03 | 4 | 0 | 0.00 | | | |
| 1,2-Dichlorobenzene | 0.57 | 0.01 | 6 | 0 | 0.00 | | | |
| *p*-Dichlorobenzene | 0.54 | 0.02 | 3 | 0 | 0.00 | | | |
| Diethylether | 0.03 | 0.03 | 11 | 0 | 0.00 | | | |
| Dipropylether | 0.03 | 0.03 | 8 | 0 | 0.00 | | | |
| Di(isopropyl) ether | 0.03 | 0 | 3 | 0 | 0.00 | | | |
| di-*n*-butyl ether | 0.04 | 0.04 | 11 | 0 | 0.00 | | | |
| Dioxane | 0.45 | 0.03 | 3 | 0 | 0.00 | | | |
| Nitromethane | 0.67 | 0.02 | 11 | 0 | 0.06 | 0.02 | 12 | 0 |
| Nitroethane | 0.66 | 0.03 | 11 | 0 | 0.00 | | | |
| 1-Nitropropane | 0.65 | 0.03 | 11 | 0 | 0.00 | | | |
| Thiophene | 0.34 | 0.01 | 3 | 0 | 0.00 | | | |
| 2-Methylthiophene | 0.37 | 0.01 | 3 | 0 | 0.00 | | | |
| 2,5-Dimethylthiophene | 0.35 | 0.01 | 3 | 0 | 0.00 | | | |
| Nitrobenzene | 0.91 | 0.04 | 4 | 0 | 0.00 | | | |
| Benzyl chloride | 0.64 | 0.01 | 3 | 0 | 0.00 | | | |
| 3-Nitrotoluene | 0.88 | 0.03 | 3 | 0 | 0.00 | | | |
| Furan | 0.26 | 0.01 | 3 | 0 | 0.00 | | | |
| Allyl mercaptan | 0.28 | 0 | 3 | 0 | 0.00 | | | |
| Tetrahydrofuran | 0.27 | 0.03 | 8 | 0 | 0.00 | | | |
| Phenylethyne | 0.47 | 0.02 | 3 | 0 | 0.09 | 0.02 | 3 | 0 |
| Anisole | 0.52 | 0.02 | 7 | 0 | 0.00 | | | |
| Pyridine | 0.60 | 0.04 | 6 | 0 | 0.00 | | | |
| Benzonitrile | 0.85 | 0.06 | 11 | 0 | 0.00 | | | |
| Benzaldehyde | 0.75 | 0.03 | 11 | 0 | 0.00 | | | |
| Acetophenone | 0.80 | 0.01 | 5 | 0 | 0.00 | | | |
| N,N-Dimethylaniline | 0.57 | 0.02 | 8 | 0 | 0.00 | | | |
| Phenol | 0.77 | 0.03 | 5 | 0 | 0.69 | 0.05 | 3 | 0 |
| Aniline | 0.76 | 0.04 | 8 | 0 | 0.20 | 0.05 | 8 | 0 |
| *m*-Cresol | 0.78 | 0.05 | 4 | 0 | 0.66 | 0.01 | 2 | 0 |
| Benzylalcohol | 0.71 | 0.05 | 6 | 1 | 0.43 | 0.06 | 9 | 0 |
| N-Methylaniline | 0.70 | 0.05 | 8 | 0 | 0.14 | 0.04 | 8 | 0 |
| Triethylamine | 0.02 | 0.02 | 6 | 0 | 0.00 | | | |
| Dimethylsulfoxide | 1.00 | 0.03 | 7 | 0 | 0.00 | | | |
| Dimethylacetamide | 0.80 | 0.04 | 8 | 0 | 0.00 | | | |
| Dimethylformamide | 0.81 | 0.02 | 8 | 0 | 0.00 | | | |
| Trifluoroethanol | 0.37 | 0.09 | 8 | 0 | 0.66 | 0.04 | 8 | 0 |
| Hexafluoroisopropanol | 0.47 | 0.07 | 5 | 0 | 1.11 | 0.06 | 6 | 0 |
| Ethylamine | 0.17 | 0.04 | 4 | 0 | 0.00 | | | |
| Propylamine | 0.22 | 0.02 | 4 | 0 | 0.00 | | | |
| Butylamine | 0.26 | 0.02 | 4 | 0 | 0.00 | | | |

The final parameter value.
Standard deviation in $\pi_2^{*,C}$ between all phases.
Number of phases used to generate $\pi_2^{*,C}$.
Number of phases for which the deviation in $\pi_2^{*,C}$ for that phase exceeds 2 S.D.
Standard deviation in $\alpha_2^C$ between all phases.
Number of phases used to generate $\alpha_2^C$.
Number of phases for which the deviation in $\alpha_2^C$ for that phase exceeds 2 S.D.

fundamental significance? As shown below the new $\pi_2^{*,C}$ and $\alpha_2^C$ are reasonably well correlated with the initial values used to establish them:

$$\pi_2^{*,C} = (-0.11 \pm 0.02) + (0.91 \pm 0.03)\pi_2^* \tag{7}$$
$$n = 203, \text{S.D.} = 0.101, r = 0.919$$

$$\alpha_2^C = (-0.01 \pm 0.003) + (1.06 \pm 0.02)\,\alpha_2^H \tag{8}$$
$$n = 203, \text{S.D.} = 0.041, r = 0.976$$

Plots of $\pi_2^{*,C}$ *versus* $\pi_2^*$ and $\alpha_2^C$ *versus* $\alpha_2^H$ are shown in Figs. 2 and 3. In Fig. 2, $\pi_2^{*,C}$ is plotted against $\pi_2^*$ for nine homologous series with different symbols for the different series. According to Abraham's estimation rule, within a given series, all $\pi_2^*$ are the same, however, we found that their $\pi_2^{*,C}$ are not constant. This is a very significant difference, we will discuss this issue in great detail below, however, we point out here that $\pi^*$ values in homologous series of solvents are different.

### $\alpha_2^C$ Values

Abraham took $\alpha_2^H$ as being the same for all higher homologues. We found that within the reliability of the measurement $\alpha_2^C$ is the same for all homologous alcohols. Even though the column-to-column variation in $\alpha_2^C$ for the carboxylic acids is large (0.05) there is a definite decrease in $\alpha_2^C$ with homologue number (acetic acid, $\alpha_2^C = 0.72$,
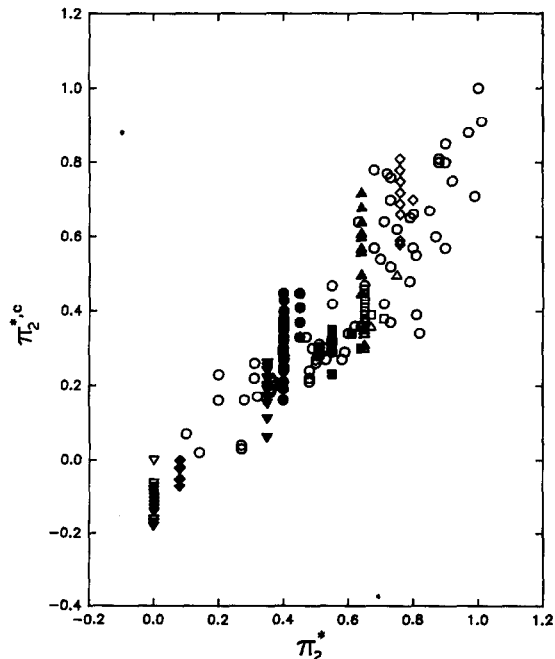


Fig. 2. $\pi_2^{*,C}$ *versus* $\pi_2^*$. $\blacklozenge$ = Alkenes; $\diamond$ = cyclic ketones; $\blacktriangle$ = carboxylic acids; $\triangle$ = aldehydes; $\blacksquare$ = nitriles; $\square$ = ketones; $\blacktriangledown$ = thiols; $\triangledown$ = alkanes; $\bullet$ = alcohols and $\circ$ = all other classes.
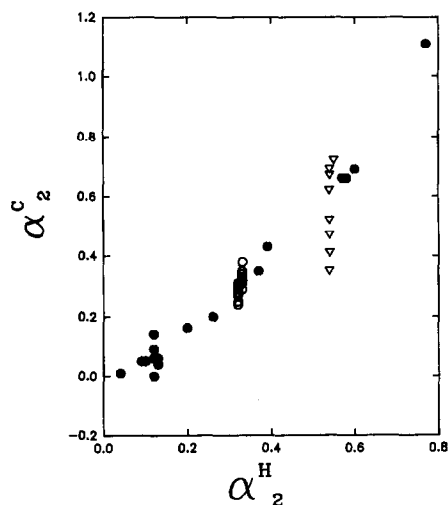
Fig. 3. $\alpha_2^C$ *versus* $\alpha_2^H$. $\bigcirc$ = Alcohols; $\nabla$ = carboxylic acids and $\bullet$ = other hydrogen bond donors.

nonanoic acid $\alpha_2^C = 0.35$). Chemically it seems most unreasonable that the hydrogen bond acidity of a –COOH group would decrease so much as the number of $CH_2$ groups increases. Certainly we expect some tendency for propanoic acid to be a slightly weaker hydrogen bond acid than acetic acid because the ethyl group is a slightly better electron donor than a methyl group. Beyond butanoic acid we expect no further decrease in hydrogen bond acidity. At this time we believe that $\alpha_2^C$ values for the higher carboxylic acids may be wrong. Indeed, we are very concerned that the $\alpha_2^C$ values for all carboxylic acids are incorrect. There are at least four reasons why this is likely. First, carboxylic acid dimerize extensively in non-polar solvents. We are not certain that this dimerization did not occur in hexadecane which is the basis for the log $L^{16}$ scale. Second, these are extremely polar compounds and in some of the phases gas–liquid interfacial adsorption may influence their retention. Third, carboxylates have a strong tendency to adsorb on diatomaceous earth. Finally, the carboxylic acid peaks were often asymmetric and the peak maximum shifted with the amount injected.

When the carboxylic acids were deleted from the correlation the following relationship is obtained:

$$\alpha_2^C = (-0.01 \pm 0.003) + (1.06 \pm 0.02)\, \alpha_2^H \qquad (9)$$
$$n = 194,\ \text{S.D.} = 0.032,\ r = 0.979$$

This result indicates that globally $\alpha_2^C$ and $\alpha_2^H$ are almost indistinguishable since the intercept is zero and the slope is nearly unity. The significant improvement in the fits when the two sets of parameters are replaced ($\pi_2^{*,C}$ *vs.* $\pi_2^*$, $\alpha_2^C$ *vs.* $\alpha_2^H$, see Table IV) is due primarily to the differences between $\pi_2^{*,C}$ and $\pi_2^*$. This is evident from the fact that the correlation of $\pi_2^{*,C}$ with $\pi_2^*$ is weaker than the correlation of $\alpha_2^C$ with $\alpha_2^H$ (see eqns. 7 and 8).

*Test of $\pi_2^{*,C}$ as a model parameter*

The above correlations show that $\pi_2^{*,C}$ and $\alpha_2^C$ are measuring approximately the same solute properties as are $\pi_2^*$ and $\alpha_2^H$. To further test the $\pi_2^{*,C}$ parameter we compared how $\pi_2^{*,C}$ and $\pi_2^*$ are related to the solute dipole moment ($\mu$) and polarizability. Our analysis is not aimed at understanding the exact dependencies but is only a comparison of the two scales for the non-HBD ($\alpha_2^C = 0$) compounds. First, we note that comparison in terms of $\mu^2$ indicates that the $\pi_2^{*,C}$ is only slightly better than $\pi_2^*$ as measured by Ehrenson's F-statistic [48].

$$\pi_2^{*,C} = (0.08 \pm 0.02) + (0.05 \pm 0.004)\,\mu^2 \tag{10}$$
$$n = 123, \text{S.D.} = 0.162, r = 0.780$$

$$\pi_2^* = (0.25 \pm 0.02) + (0.05 \pm 0.004)\,\mu^2 \tag{11}$$
$$n = 123, \text{S.D.} = 0.174, r = 0.768$$
$$R = 1.092 > R_{1,122,0.95} = 1.033$$

Next we added the polarizability parameter ($R_2$) proposed by Abraham [37],

$$\pi_2^{*,C} = (-0.04 \pm 0.02) + (0.043 \pm 0.002)\,\mu^2 + (0.49 \pm 0.04)\,R_2 \tag{12}$$
$$n = 123, \text{S.D.} = 0.107, r = 0.911$$

$$\pi_2^* = (0.14 \pm 0.02) + (0.045 \pm 0.003)\,\mu^2 + (0.43 \pm 0.05)\,R_2 \tag{13}$$
$$n = 123, \text{S.D.} = 0.138, r = 0.862$$
$$R = 1.285 > R_{2,121,0.95} = 1.051$$

We see that both correlations improved and the correlation of $\pi_2^{*,C}$ is statistically superior to that of $\pi_2^*$. This is an important observation. Clearly our $\pi_2^{*,C}$ and $\alpha_2^C$ values fit the retention data with much better precision than do $\pi_2^*$ and $\alpha_2^H$. However, they must do so as they are derived from the retention data. Thus the better fits to chromatographic data provide no evidence that the new parameters are in anyway superior to $\pi_2^*$ and $\alpha_2^H$. However, the fact that $\pi_2^{*,C}$ is better fit to a reasonable dependence on dipole moment and polarizability than is $\pi_2^*$ provides independent support for its use and physical significance.

*Test of the fitting coefficients*

A second approach to testing the new parameters is to assess whether the coefficients ($s,a$) of the final regressions of log $k'$ *versus* the explanatory variables make chemical sense. As pointed out above, according to the solvatochromic LSER method [22,24], a stationary phase with a high bulk phase $\pi_{\text{solvent}}^*$ (denoted $\pi^*$) must have a high $s$ coefficient. Smilarly a very basic stationary phase, that is, one whose bulk phase hydrogen bond basicity $\beta_{\text{solvent}}$ (denoted $\beta$) is high must have a high $a$ coefficient. To this end the bulk $\pi^*$ and $\beta$ parameters of the low-molecular-weight phases (in data bases B and C) were directly evaluated by the solvatochromic comparison method. Details of this work will be reported elsewhere. However, we are compelled to point out that we computed the solvent $\pi^*$ by reference to the frequency of maximum

absorption of the indicator in cyclohexane and DMSO at 25°C. Since the phase $s$ and $a$ coefficients were measured at a variety of temperatures (often higher than 100°C), we measured $\pi^*$ and $\beta$ at fairly high temperatures (70–90°C) and extrapolated them to the temperature of interest. As might be expected the temperature dependence of $\pi^*$ and $\beta$ are difficult to define precisely, thus based on our work and that of Laurence and co-workers [49,50] we used an average temperature coefficient of $-0.0017/°C$ for both $\pi^*$ and $\beta$ for all solvents. The LSER coefficients ($s$ and $a$) for the phases (shown in Table VI) were plotted against the extrapolated values of $\pi^*$ and $\beta$ for these solvents (see Figs. 4–7) at the column temperature. Evidently there is a somewhat tighter correlation between $s$ and $\pi^*$ when we use the new solute parameters $\pi_2^{*,C}$ rather than when $\pi_2^*$ was used. For $\pi_2^{*,C}$ and $\pi_2^*$, the results are as follows:

$$s\,(\pi_2^{*,C}) = (-0.04 \pm 0.09) + (2.56 \pm 0.18)\,\pi^* \tag{14}$$
$$n = 10,\ \text{S.D.} = 0.15,\ r = 0.981$$

$$s\,(\pi_2^*) = (-0.02 \pm 0.11) + (2.25 \pm 0.22)\,\pi^* \tag{15}$$
$$n = 10,\ \text{S.D.} = 0.18,\ r = 0.964$$
$$R = 1.220 > R_{1,9,0.90} = 1.172$$

We are very pleased to note that the intercept of these plots are quite small. As one

TABLE VI

COMPARISON OF THE INITIAL AND FINAL REGRESSION RESULTS

Eqn. 6 is the regression equation employed.

| Phase | | | $XYZ_0$ | $l$ | $s$ | $b$ | $d$ | $a$ |
|---|---|---|---|---|---|---|---|---|
| TEHP | 1 | Initial | −0.014 | 0.580 | 0.880 | −0.268 | −0.179 | 2.131 |
| | 2 | Final | 0.304 | 0.521 | 0.889 | −0.230 | −0.073 | 1.816 |
| TOPO | 1 | | −1.954 | 0.667 | 0.997 | −0.103 | −0.136 | 4.103 |
| | 2 | | −1.564 | 0.608 | 1.158 | −0.288 | −0.100 | 3.810 |
| DEDA | 1 | | −1.685 | 0.755 | 1.117 | −0.181 | −0.198 | 2.917 |
| | 2 | | −1.348 | 0.706 | 1.176 | −0.168 | −0.115 | 2.440 |
| DMDA | 1 | | −1.607 | 0.912 | 0.602 | −0.319 | −0.197 | 2.845 |
| | 2 | | −1.365 | 0.859 | 0.558 | −0.178 | −0.090 | 2.507 |
| MDOA | 1 | | −1.587 | 0.838 | 0.178 | 0.006 | −0.044 | 1.440 |
| | 2 | | −1.473 | 0.812 | 0.255 | −0.095 | −0.036 | 1.533 |
| BPP | 1 | | −1.863 | 0.817 | 1.031 | −0.135 | −0.197 | 2.980 |
| | 2 | | −1.557 | 0.772 | 1.069 | −0.072 | −0.126 | 2.523 |
| ZE7 | 1 | | −2.093 | 0.434 | 1.161 | 0.599 | −0.052 | 0.509 |
| | 2 | | −1.784 | 0.394 | 1.251 | 0.640 | −0.051 | 0.203 |
| Carbowax | 1 | | −2.050 | 0.446 | 1.529 | −0.142 | 0.056 | 2.066 |
| | 2 | | −1.624 | 0.388 | 1.676 | −0.071 | 0.048 | 1.468 |
| TCEP | 1 | | −1.730 | 0.379 | 2.022 | 0.326 | 0.080 | 1.727 |
| | 2 | | −1.173 | 0.305 | 2.247 | 0.374 | 0.059 | 1.024 |
| PPE6 | 1 | | −2.536 | 0.554 | 0.992 | 0.100 | 0.042 | 0.488 |
| | 2 | | −2.255 | 0.516 | 1.190 | 0.031 | 0.008 | 0.179 |
| DEGS | 1 | | −1.804 | 0.399 | 1.728 | 0.154 | 0.127 | 1.765 |
| | 2 | | −1.317 | 0.333 | 1.979 | 0.143 | 0.093 | 1.134 |

hopes when the $\pi^*$ of the stationary phase is zero the phase $s$ value is very small. In fact the $\pi^*$ of $n$-hexadecane is 0.08, its $s$ value is zero by definition. Eqn. 14 predicts its $s$ value to be 0.16 ($\pm$ 0.15). Similarly eqn. 15 predicts its $s$ value to be 0.16 ($\pm$ 0.18). Overall the observations reported in Figs. 4 and 5 constitute a strong qualitative verification of the basic concepts of the LSER approach.

Analysis of the correlation between $a$ and $\beta$ is more complicated. It has been shown that there is a family dependent relationship such that OH acceptors and NH acceptors act differently toward hydrogen bond donor indicators such as $p$-nitro-aniline [49]. Based on Maria $et\ al.$'s work [51], this should not be surprising. We are not convinced that there is a family dependence shown in Figs. 6 and 7. The correlation results are shown as follows:

For all phases

$$a(\alpha_2^C) = (0.09 \pm 0.16) + (2.96 \pm 0.24)\,\beta \qquad\qquad (16)$$
$$n = 10,\ \text{S.D.} = 0.25,\ r = 0.974$$

$$a(\alpha_2^H) = (0.45 \pm 0.27) + (2.99 \pm 0.41)\,\beta \qquad\qquad (17)$$
$$n = 10,\ \text{S.D.} = 0.42,\ r = 0.933$$
$$R = 1.679 > R_{1,9,0.90} = 1.172$$

We note that as required by the LSER formalism the $a$ coefficient is zero when the solvent $\beta$ is zero. Again this provides excellent support for the LSER approach. We note that $a$ based on the $\alpha_2^C$ scale is somewhat superior to the $\alpha_2^H$ scale. Given the paucity of the data we do not insist that the correlations based on $\pi_2^{*,C}$ and $\alpha_2^C$ are better than $\pi_2^*$ and $\alpha_2^H$. However, we certainly have not achieved the much superior fits of the retention data at the cost of introducing chemically meaningless values of the LSER fitting coefficients ($s$, $a$).
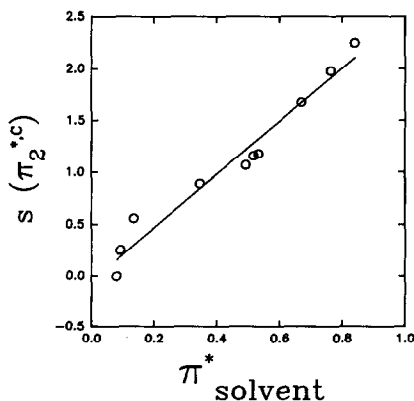


Fig. 4. $s(\pi_2^{*,C})$ $versus$ $\pi_{solvent}^*$.
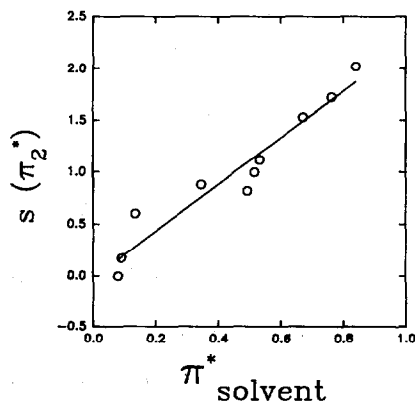
Fig. 5. $s(\pi_2^*)$ $versus$ $\pi_{solvent}^*$.
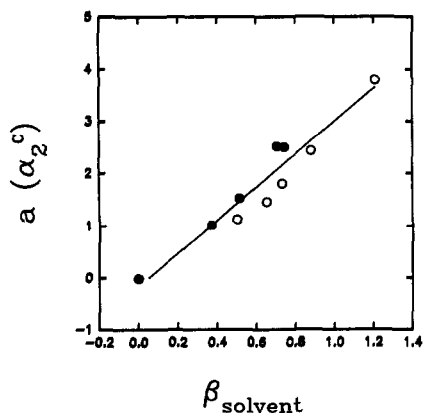
Fig. 6. $a(\alpha_2^C)$ versus $\beta_{solvent}$. O = Oxygen base and ● = nitrogen base.
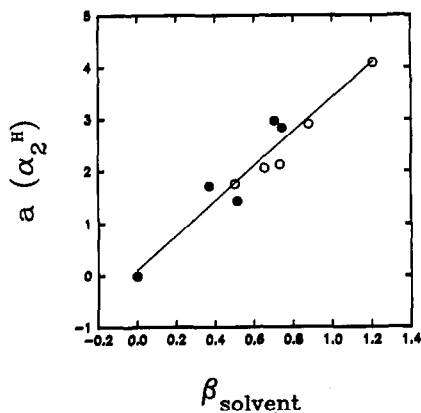
Fig. 7. $a(\alpha_2^H)$ versus $\beta_{solvent}$. O = Oxygen base and ● = nitrogen base.

## Generality of the new parameters

The question naturally arises as to whether the solute parameters determined here are applicable only within the context of gas chromatographic retention. Can they be used with good results in other types of correlations? The issue of the universality of solvatochromic LSER methods has been extensively discussed by Kamlet and Taft [52] and Sjöström and Wold [53]. The most extensive data set yet reported by the Kamlet group is that pertaining to the study of octanol–water partition coefficients [25]. Reexamination of this data set does not constitute a severe test of the new parameters since $K_{ow}$ is strongly dependent on solute size and hydrogen bond basicity and only weakly dependent on dipolarity and hydrogen bond acidity. Nonetheless for the intersection of our solute sets, we obtained the following results:

Using our parameters:

$$\log K_{ow} = -0.03 + 5.72\ V_1 - 0.84\pi_2^{*,C} + 0.16\delta - 4.19\beta_m + 0.44\alpha_2^C \quad (18)$$

$$n = 63, \text{S.D.} = 0.083, r = 0.9984$$

Using Abraham's parameters:

$$\log K_{ow} = 0.26 + 5.56V_1 - 0.83\pi_2^* + 0.15\delta - 4.26\beta_m + 0.20\alpha_2^H \quad (19)$$

$$n = 63, \text{S.D.} = 0.084, r = 0.9984$$

Using the original Kamlet's parameters

$$\log K_{ow} = 0.25 + 5.54V_1 - 0.88\pi^* + 0.20\delta - 4.18\beta_m + 0.15\alpha_m \quad (20)$$

$$n = 63, \text{S.D.} = 0.085, r = 0.9984$$

where $\beta_m$ is the hydrogen bond basicity of a monomeric species and was developed by Kamlet and co-workers [54,55] to specifically fit solubility in water, $K_{ow}$ values and

retention in reversed-phase liquid chromatography. From the above, we can see that using either Abraham's parameters ($\pi_2^*$ and $\alpha_2^H$) or our parameters ($\pi_2^{*,C}$ and $\alpha_2^C$) give essentially the same results in terms of the goodness of fit as well as the sign and the magnitude of the regression coefficients.

We conclude that no harm will result in correlating properties related to transfer from water to less polar media, such as capacity factors in reversed-phase liquid chromatography, solubility of organic compounds in water etc., by use of the new parameters. At the same time the new parameters, in contrast to the "old" parameters, give excellent fits to GC retention data.

*Test of the homologue dependence of $\pi_2^{*,C}$ and the Martin equation*

Plots of $\pi_2^{*,C}$ vs. homologue number (HN) are shown in Fig. 8. In most cases the $\pi_2^{*,C}$ values increase more or less monotonically with the number of methylene groups in the solute. There is clearly a great deal of scatter and in one case (olefins) the $\pi_2^{*,C}$ actually decreases with increasing number of methylene groups. At this point, we are not sure if the $\pi_2^{*,C}$ for the olefins are correct. These trends in $\pi_2^{*,C}$ are somewhat disturbing. As will be shown below in any series where $\pi_2^{*,C}$ is independent of homologue number the Martin equation (see below) must be valid. In contrast it is not clear whether a monotonic or highly scattered relationship between $\pi_2^{*,C}$ and HN will be consistent with the Martin equation.

The Martin equation is a very widely accepted *experimental* observation. It indicates that the logarithmic partition coefficient or the logarithmic capacity factor is, within a homologous series, a linear function of the number of carbon atoms in the specific homologue:

$$\log k' \text{ (or } K \text{ or } L') = A + B \text{ HN} \tag{21}$$

Theoretically the Martin equation cannot be exact because of size dependent configurational contributions to the free energy of gas to liquid transfer that are not
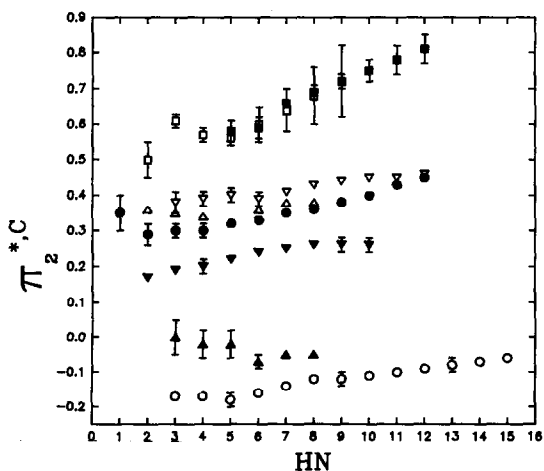


Fig. 8. $\pi_2^{*,C}$ *versus* homologue number (HN) for eight homologous series. $\bigcirc$ = Alkanes; $\bullet$ = alcohols; $\nabla$ = 2-ketones; $\blacktriangledown$ = thiols; $\square$ carboxylic acids; $\blacksquare$ = cycloketones; $\triangle$ = aldehydes and $\blacktriangle$ = alkenes.

linear with HN. Relatively simple models of the solution process such as UNIFAC [56] show that there cannot be precise linearity with HN values. More advanced models such as Martire's [57,58] application of Sanchez–Lacombe lattice theory [59] to gas chromatography also show that the Martin equation is an approximate result. Any reasonable model of retention must be, at least approximately, in agreement with the Martin equation and any model which predicts significant deviations is inherently dubious.

It is easily shown that Abraham's set of solute parameters (Table I) must be in accord with the Martin equation. He assigned, in a given series, the same values to $\pi_2^*$, $\beta_2^H$ and $\alpha_2^H$ for all higher homologues. Thus for a specific homologous series the only variable term in the LSER equation governing the variations in $k'$ from homologue to homologue generated by Abraham's approach is the $\log L^{16}$. Consequently, within a series the LSER can be written as:

$$\log k'_{\text{homo,Abraham}} = XYZ'_0 + l \log L^{16} \tag{22}$$

where $XYZ'_0$ is defined as:

$$XYZ'_0 = XYZ_0 + s\pi^*_{2,\text{homologue}} + a\alpha^H_{2,\text{homologue}} + b\beta^H_{2,\text{homologue}} \tag{23}$$

As shown in Fig. 9 $\log L^{16}$ is a linear function of HN. Thus eqn. 22 correctly predicts that $\log k'$ is a linear function of HN since as shown in Table VII for some 16 different homologous series, $\log L^{16}$ is a quite linear function of carbon number. It should be noted that for $\log L^{16}$ the slope of the homologous plot (B in eqn. 21) differs from series-to-series (see Table VII). However, these differences in slope $B$ are small relative to the analogous differences observed on more polar columns. It follows from eqns. 22 and 23 that on any stationary phase the Abraham parameter set predicts that the differences in slope $B$ for $\log L'$ from homologous series to homologous series will be
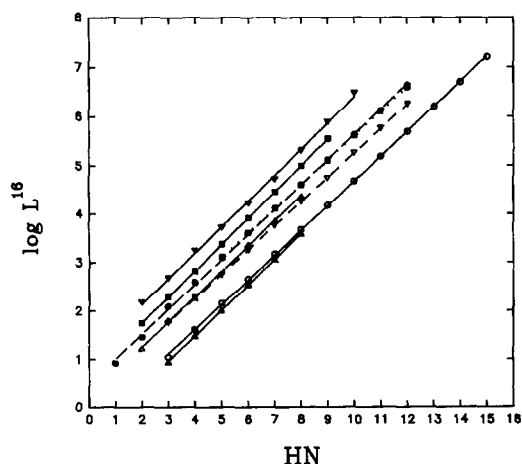


Fig. 9. log $L^{16}$ versus HN for eight homologous series. $\bigcirc$ = Alkanes; $\bullet$ = alcohols; $\nabla$ = 2-ketones; $\blacktriangledown$ = thiols; $\square$ = cycloketones; $\blacksquare$ = carboxylic acids; $\triangle$ = aldehydes and $\blacktriangle$ = alkenes.

TABLE VII

CORRELATION RESULTS OF LOG $L^{16}$ VS. CARBON NUMBER FOR HOMOLOGOUS SERIES

Eqn. 21 is the regression equation employed.

| Homologues | Series No. | $n$ | Range | $A$ | S.D. | $r^2$ | $B$ |
|---|---|---|---|---|---|---|---|
| Alkanes | 1 | 13 | 3–15 | −0.4144 | 0.0249 | 0.9999 | 0.5094 0.0018[a] |
| Alcohols | 2 | 12 | 1–12 | 0.4904 | 00463 | 0.9994 | 0.5150 0.0039 |
| 2-Ketones | 3 | 10 | 3–12 | 0.2701 | 0.0091 | 1.0000 | 0.4989 0.0010 |
| Thiols | 4 | 9 | 2–10 | 1.0730 | 0.0531 | 0.9988 | 0.5330 0.0069 |
| Carboxylic acids | 5 | 8 | 2–9 | 0.6631 | 0.0032 | 1.0000 | 0.5426 0.0005 |
| Cycloketones | 6 | 8 | 5–12 | 0.6280 | 0.0031 | 1.0000 | 0.4980 0.0005 |
| Aldehydes | 7 | 6 | 2–8 | 0.2065 | 0.0304 | 0.9995 | 0.5229 0.0057 |
| Alkenes | 8 | 6 | 3–8 | −0.6280 | 0.0078 | 0.9999 | 0.5279 0.0019 |
| Acetates | 9 | 5 | 1–5 | 1.4697 | 0.0289 | 0.9989 | 0.4703 0.0091 |
| Sulfides | 10 | 4 | 2–8 | 1.3150 | 0.0546 | 0.9986 | 0.4576 0.0122 |
| Alkylbenzenes | 11 | 5 | 6–10 | −0.0006 | 0.0296 | 0.9988 | 0.4717 0.0094 |
| Nitriles | 12 | 4 | 2–5 | 0.5152 | 0.0460 | 0.9967 | 0.5053 0.0206 |
| Nitroaliphatics | 13 | 3 | 1–3 | 1.4117 | 0.0033 | 1.0000 | 0.4790 0.0023 |
| Amines | 14 | 3 | 2–4 | 0.7338 | 0.0053 | 0.9999 | 0.4705 0.0038 |
| Ethers | 15 | 3 | 4–8 | 0.1010 | 0.0490 | 0.9987 | 0.4850 0.0173 |
| Cycloalkanes | 16 | 3 | 5–7 | −0.3903 | 0.0584 | 0.9946 | 0.5585 0.0413 |

[a] Standard deviation of the slope.

small and in proportion to their $B$ coefficient for log $L^{16}$. As shown in Fig. 10, this is not the case, that is, the ratio of the $B$ coefficients for log $L'$ and log $L^{16}$ is not constant for different homologous series on any given column.

   We wish to comment here on whether one should expect to see changes between different homologous series in the slopes of plots of log $L^{16}$ vs. HN as shown in Fig. 9. Are these changes real or are they due to experimental problems such as interfacial adsorption? In order to assess the validity of the slopes we can compare them to slopes predicted based on a theoretical model of the solution process. Although the UNIFAC model is not highly accurate [56], it can give us a reasonable estimate especially in a system as chemically simple as these solutes in hexadecane. The partition coefficients
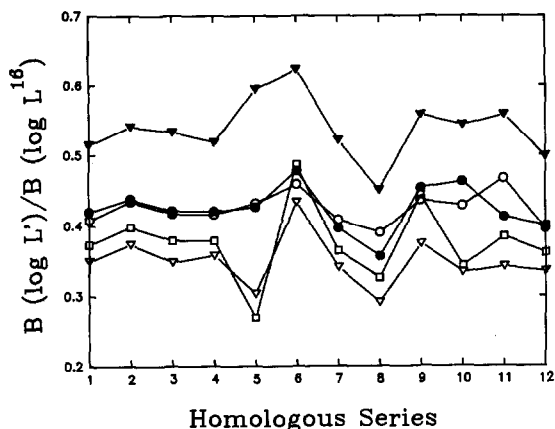
Fig. 10. Plots of the ratio of the slopes of log $L'$ *vs.* HN and log $L^{16}$ *vs.* HN for 12 homologous series on 5 columns. Homologous series numbers are the same as in Table VII. ▼ = PPE6; ○ = ZE7; ● = Carbowax; ▽ = TCEP and □ = DEGS.

can be computed from knowledge of the vapor pressures ($P_2$), estimates of the activity coefficients ($\gamma_2^\infty$), molar volume ($V_m$) and the following equation:

$$K = RT/\gamma^\infty P_2 V_m \tag{24}$$

The slopes of computed plots of log $K^{16}$ *vs.* HN for several homologous series and of log $L^{16}$ are shown in Fig. 11. We also give slopes of plots of log $P_2$ *vs.* HN for reference purposes. From these results, it is clear that one should not expect the same slopes for plots of log $L^{16}$ *vs.* HN for different homologous series. Plots of the logarithm of the retention volume of different compounds *versus* the number of $CH_2$ in their alkyl chain by Ray [60] supports this conclusion. Finally, measurement of a large number of gas–liquid partition coefficients of homologous series of solutes in hexadecane by
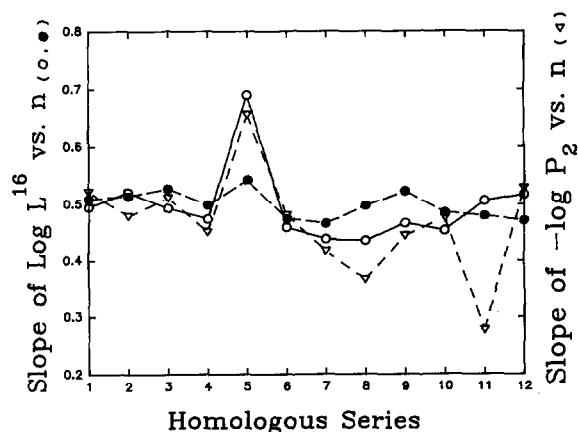


Fig. 11. Plots of UNIFAC predicted (○) and experimental (●) slopes of log $L^{16}$ *vs.* HN and $-\log P_2$ (vapor pressure at 25°C, torr) *vs.* HN (▽) for 12 homologous series. Homologous series No.: 1 = Alkanes; 2 = alcohols; 3 = alkenes; 4 = 2-ketones; 5 = carboxylic acids; 6 = alkylbenzenes; 7 = acetates; 8 = nitriles; 9 = aldehydes; 10 = ethers; 11 = nitroaliphatics and 12 = amines.

head-space gas chromatography, which is not subject to all of the interfacial adsorption problems of the dynamic GC approach, confirm the variation in these slopes [61].

*New parameters and the Martin equation*

Inspection of our set of parameters (Table V) shows that in most homologous series (see, for example the alkanes, alcohols, 2-alkanones) there are significant variations in the parameters with HN. In general our parameters are neither fixed within a series nor are they strictly linear with HN. Thus we *do not* predict an *exact linear relationship* between log $k'$ and carbon number and we are seemingly in disagreement with the Martin equation. However, this lack of agreement is only apparent (see below). It will turn out that our parameters, are, within any reasonable expectation of the experimental precision, in accord with the Martin equation. More importantly because the parameters vary within a homologous series we do not predict that all homologous series will produce the same ratio of slopes of log $k'$ *vs.* HN relative to the slope of log $L^{16}$ *vs.* HN (see Fig. 10).

The two different sets of parameters ($\pi_2^{*,C}$ and $\pi_2^*$) were examined by comparing the measured and computed capacity factors for a variety of homologous series of solutes on a set of phases that are chemically very distinct. We are not in a position to compare $\alpha_2^C$ and $\alpha_2^H$ because we really only have two homologous series (alcohols and carboxylic acids) of hydrogen bond donors.

First, let us show that our $\pi_2^{*,C}$ values are in good agreement with the Martin equation. To do so we will use the cycloalkanones since they show the largest change in $\pi_2^{*,C}$ of any series. Note that for a series in which the change in $\pi_2^{*,C}$ is zero exact agreement with the Martin equation is predicted so this does not constitute a useful test. Second, if the stationary phase has a small $s$ coefficient the effect of $\pi_2^{*,C}$ on retention will be small. The Carbowax column was chosen because it is a fairly common stationary phase and has a rather high $s$ coefficient (see Table VI). The log $k'$ values predicted by $\pi_2^{*,C}$, by Abraham's $\pi_2^*$, and the experimental values are shown in Fig. 12. It is evident that our results, as are Abraham's, are in good agreement with the
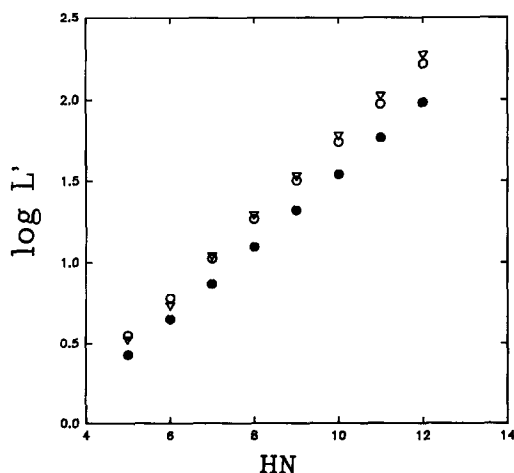


Fig. 12. Plots of experimental and predicted log $L'$ versus HN for cycloketones on the Carbowax column. $\bigcirc$ = Experimental; $\bullet$ = Abraham and $\nabla$ = this work.

Martin equation, that is, they predict a linear dependence of log $k'$ on HN. Clearly our results are in better agreement with the experimental data. These results are quite typical of a large number of such plots for many homologous series on a variety of stationary phases. That is, our $\pi_2^{*,C}$ parameter predicts retention variation with HN that are in better agreement with the measured $k'$ values than are the old $\pi_2^*$ parameters.

We next compare the accuracy of prediction of the slope of plots of log $k'$ vs. HN for a variety of homologous series on different columns. These results are shown in Figs. 13 and 14 as the ratio of the predicted slope to the experimental slope. Obviously this ratio should be unity. The results for different columns are offset by exactly 1.0 unit. Comparison of Fig. 13 to 14 shows that, in general, $\pi_2^{*,C}$ is better than $\pi_2^*$. We conclude that the new $\pi_2^{*,C}$ is generally in better agreement with the Martin equation and the actual data than the $\pi_2^*$ parameter when the data are compared either in general or when compared in terms of individual homologous series.

Although not relevant to testing concordance with the Martin equation we can also examine the intercepts predicted by the LSER approach to the experimental intercepts. This was done in the same fashion as the slopes. The results are similar to the slopes (not shown). It is clear that overall the $\pi_2^{*,C}$ parameter produces better agreement with experiment than the $\pi_2^*$ parameter.

*Use of the Martin equation to estimate $\pi_2^{*,C}$ values*

Based on the observed consistency of the LSER approach and the Martin equation, at least for the non-hydrogen bond donor solutes, one can use the consistency to smooth the available data and estimate additional solutes in a homologous series for which some data exist. We use this idea to generate our final recommended values for $\pi_2^{*,C}$ (Table VIII). For non-hydrogen bond donor solutes on a non-acidic phase the approach is as follows. First, obtain $l$, $s$, $a$, $b$ and $d$ as above. Second, regress log $k'$ vs. HN for the homologous series of interest to obtain the conventional least
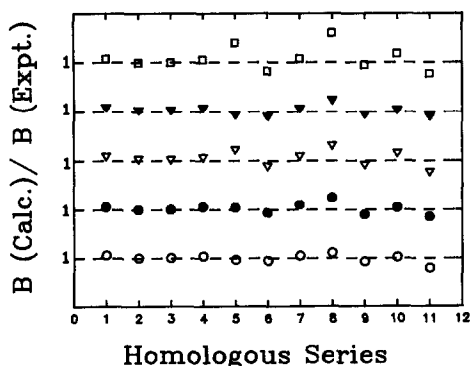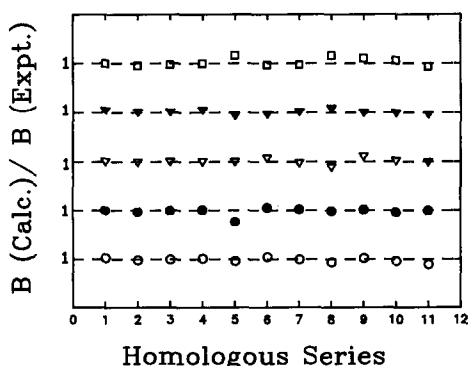


Fig. 13. Plots of the ratio of slopes of log $L'$ vs. HN predicted by present work and experimental values for 11 homologous series on 5 columns. Homologous series numbers are the same as in Table VII. ○ = ZE7; ● = Carbowax; ∇ = TCEP; ▼ = PPE6 and □ = DEGS.

Fig. 14. Plots of the ratio of slopes of log $L'$ vs. HN predicted by Abraham and experimental values for 11 homologous series on 5 columns. Homologous series numbers and symbols are the same as in Fig. 13.

TABLE VIII

FINAL RECOMMENDED VALUES FOR $\pi_2^{*,C}$

| No. | Compound | $\pi_2^{*,C}$ |
|-----|----------|---------------|
| 24 | 1-Butene | −0.02 |
| 25 | 1-Pentene | −0.03 |
| 26 | 1-Hexene | −0.04 |
| 27 | 1-Heptene | −0.05 |
| 42 | 1-Hexanol | 0.33 |
| 43 | 1-Heptanol | 0.35 |
| 44 | 1-Octanol | 0.37 |
| 45 | 1-Nonanol | 0.39 |
| 46 | 1-Decanol | 0.41 |
| 47 | 1-Undecanol | 0.43 |
| 48 | 1-Dodecanol | 0.45 |
| 68 | $n$-Pentanethiol | 0.22 |
| 70 | $n$-Hexanethiol | 0.23 |
| 71 | $n$-Heptanethiol | 0.24 |
| 72 | $n$-Octanethiol | 0.25 |
| 73 | $n$-Nonanethiol | 0.26 |
| 74 | $n$-Decanethiol | 0.27 |
| 78 | 2-Pentanone | 0.40 |
| 80 | 2-Hexanone | 0.41 |
| 81 | 2-Heptanone | 0.42 |
| 82 | 2-Octanone | 0.43 |
| 83 | 2-Nonanone | 0.44 |
| 84 | 2-Decanone | 0.45 |
| 85 | 2-Undecanone | 0.46 |
| 86 | 2-Dodecanone | 0.47 |
| 90 | Cycloheptanone | 0.66 |
| 91 | Cyclooctanone | 0.69 |
| 92 | Cyclononanone | 0.72 |
| 93 | Cyclodecanone | 0.75 |
| 94 | Cycloundecanone | 0.78 |
| 95 | Cyclododecanone | 0.81 |
| 132 | $n$-Propyl acetate | 0.31 |
| 133 | $n$-Butyl acetate | 0.33 |
| 134 | $n$-Pentyl acetate | 0.35 |
| 141 | Propionaldehyde | 0.34 |
| 142 | Butyraldehyde | 0.35 |
| 145 | Hexanal | 0.36 |
| 146 | Heptanal | 0.37 |
| 147 | Octanal | 0.38 |
| 151 | Toluene | 0.29 |
| 152 | Ethylbenzene | 0.30 |
| 156 | Propylbenzene | 0.31 |
| 157 | Butylbenzene | 0.32 |

squares slope and intercept for the Martin equation ($A$ and $B$ in eqn. 21). Third, compute the slope of $\pi_2^{*,C}$ vs. HN as follows:

$$B_2 = (B - lB_1)/s \tag{25}$$

where $B_1$ is the slope of log $L^{16}$ vs. HN. Clearly this approach forces $\pi_2^{*,C}$ to be a linear

function of HN. The slope resulting from this approach is given in Table IX. Therefore, we can estimate $\pi_2^{*,C}$ by using the slope $B_2$ and a lower member's value as an intercept. Note we have given both the individual results based on a specific type of stationary phase and the average and standard deviation over all phases. For the alcohols, carboxylic acids and those compounds which are not a member of an homologous series the recommended $\pi_2^{*,C}$ value remain as in Table V.

Actually the above approach can be used to estimate $\pi_2^{*,C}$ for a homologous series of hydrogen bond donors provided that all higher members of the series have the same donor ability. This is always a good approximation. In this case the slope given in Table IX is used in conjunction with a $\pi_2^{*,C}$ value for a lower member of the series as obtained from Table V. The quality of the fits of gas chromatographic data is hardly affected by the above procedure (results are not given).

For all series (HN $> 3$), except the olefins, the average slopes of the relationship between $\pi_2^{*,C}$ and HN are positive. Within a homologous series the slope is well defined but the slopes vary rather considerably between series. As noted above the slopes of the cycloketones are quite high ($+0.03$, S.D. $= 0.007$) whereas the slope for the olefins is the lowest ($-0.01$, S.D. $= 0.01$).

The data are persuasive that $\pi_2^{*,C}$ values, as estimated from retention data, are a function of HN. In contrast we point out that measurements of dipole moments in solution are independent of HN [62]. Clearly there must be contributions to $\pi_2^{*,C}$ from factors other than the dipole moment of the species. As shown by eqns. 10 and 12 the molecular polarizability is such a factor. However, based on the fact that the change in polarizability per methylene group is virtually independent of the rest of the molecule [63] a polarizability contribution to $\pi_2^{*,C}$ cannot account for the variation in the slope of $\pi_2^{*,C}$ from series-to-series. Furthermore calculations based on the use of the Staverman–Guggenheim term of the UNIFAC method [56] show that differences in the configurational entropy per methylene groups as the homologous series is varied are much too small to be significant. We have to conclude that the $\pi_2^{*,C}$ term in this work is in part related to the inadequacy of log $L^{16}$ to simultaneously model both dispersion interactions and the cavity formation process.

TABLE IX

SLOPE OF $\pi_2^{*,C}$ *VS.* HN

| Series | B2 | | | | | | |
|---|---|---|---|---|---|---|---|
| | ZE7 | Carbowax | TCEP | PPE6 | DEGS | Avg | S.D. |
| Alkanes | 0.006 | 0.010 | 0.010 | −0.001 | 0.010 | 0.007 | 0.004 |
| 2-Ketones | 0.009 | 0.010 | 0.010 | 0.007 | 0.012 | 0.009 | 0.001 |
| Thiols | 0.010 | 0.010 | 0.012 | 0.001 | 0.012 | 0.009 | 0.004 |
| Cycloketones | 0.026 | 0.027 | 0.028 | 0.044 | 0.039 | 0.033 | 0.007 |
| Aldehydes | 0.006 | 0.003 | 0.008 | 0.002 | 0.008 | 0.005 | 0.003 |
| Alkenes | −0.002 | −0.010 | −0.003 | −0.029 | −0.002 | −0.009 | 0.010 |
| Acetates | 0.016 | 0.018 | 0.014 | 0.016 | 0.026 | 0.018 | 0.004 |
| Sulfides | 0.013 | 0.020 | 0.006 | 0.010 | 0.002 | 0.010 | 0.006 |
| Alkylbenzenes | 0.028 | 0.007 | 0.008 | 0.017 | 0.012 | 0.014 | 0.008 |
| Alcohols | 0.017 | 0.015 | 0.016 | 0.011 | 0.017 | 0.015 | 0.002 |

CONCLUSIONS

A gas chromatographically based approach to the measurement of the dipolarity/polarizability ($\pi_2^{*,C}$) and hydrogen bond donor acidity ($\alpha_2^C$) parameters has been developed. Parameters for 203 chemically very diverse species are presented. The resulting parameters naturally fit the GC retention data bases with better precision than non-chromatographically based parameters. The physical meaning of the parameters is maintained. The excellent correlations between the fitting coefficients ($s$ and $a$) and the measured $\pi^*$ and $\beta$ parameters of the stationary phases provide a great deal of support to the legitimacy of the solvatochromic approach to the interpretation of solute–solvent interactions.

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