

CHROMSYM. 1952

Empirical scheme for the classification of gas chromatographic stationary phases based on solvatochromic linear solvation energy relationships

JIANJUN LI, ANDREW J. DALLAS and PETER W. CARR*

Department of Chemistry, University of Minnesota, Kolthoff and Smith Halls, 207 Pleasant Street, Minneapolis, MN 55455 (U.S.A.)

ABSTRACT

Due to the plethora of materials that have been used as stationary phases in gas chromatography it is clearly necessary to have some method for classifying phases to facilitate systematic method development. The most popular classification scheme is the Rohrschneider–McReynolds procedure which is based on the Kováts retention indices of a variety of probe solutes. Although this is a very useful approach, it is highly empirical and has been criticized on several grounds. In this work we explored the use of solvatochromic measures of solute dipolarity-polarizability (π_2^*), hydrogen bond donor acidity (α_2) and hydrogen bond acceptor basicity (β_2) to classify a variety of common capillary gas chromatographic stationary phases. Preliminary studies show that the use of only the solvatochromic parameters as explanatory variables leads to rather poor precision. However, when log capacity factors on two extreme types of phases are included among the explanatory variables quite high precision, typically an average standard deviation of less than 0.07 log units, is obtained and all columns tested were easily classified. The two reference phases should be a low-polarity phase and a high-polarity, hydrogen bond acceptor phase.

INTRODUCTION

Currently more than 200 liquid phases suitable for use as stationary phases in gas chromatography (GC) are commercially available. This huge number of materials mandates that they be classified. Consequently it is not surprising that there have been many studies aimed at identifying and quantifying their retention characteristics. The most common of these, and perhaps that which is chemically most appealing, is the multiple probe solute method developed by Rohrschneider^{1–3} and later extended by McReynolds⁴. This approach has been used as the basis for choosing a small set of stationary phases that should accommodate a very wide variety of samples⁵. It is, however, based on the Kováts retention index scheme for quantifying retention.

Among others, Poole has criticized the Kováts index based classification methods, in part because they rely on the normalization of the retention of the polar solutes relative to the retention of *n*-alkanes^{6,7}. In essence, for polar stationary phases the change in the retention index of a polar solute relative to its value on a non-polar phase is due as much to the decrease in retention of the reference alkanes, relative to their retention on a non-polar phase, as it is to the increase in retention of the polar solute. Clearly this complicates the chemical interpretation of the change in retention index from phase to phase. To avoid or minimize this problem, many investigators⁸ have used series of homologues other than the *n*-alkanes as the basis for retention index schemes.

Other classification schemes have been investigated^{9–16}. For example, Howerly and co-workers^{9–11} have used factor analysis to classify GC phases. Laffort and Patte^{12,13} developed the use of “solubility factors” to characterize liquid stationary phases. However, because some of these classification methods are based on retention indices or they used the retention of alkanes as a reference, they suffer from some of the problems mentioned above.

In this study we used solvatochromically based linear solvation energy relationships (LSER) to explore and rationalize retention relationships on a variety of common capillary columns that span a full polarity range. This set of columns does not cover all the possible GC phases. Most notably none of the phases has strong hydrogen bond donor properties. We choose to study the properties of fused-silica based capillary columns because they have a low ratio of surface area to phase volume and afford a less sorptive underlying solid surface relative to the porous supports used in packed columns. This helps minimize interfacial adsorption effects. It should be noted that capillary columns are not entirely free of gas–liquid interfacial adsorption effects^{17–19}, nor can one disregard the potential for interaction with the silica surface.

The solvatochromic parameters used in this work are the Kamlet–Taft solute dipolarity-polarizability (π_2^*), hydrogen bond donor acidity (α_2) and hydrogen bond acceptor basicity (β_2). The solute parameter is different from the solvent parameter and is differentiated from a solvent parameter by a subscript 2. The dipolarity-polarizability scale (π^* or π_2^*) is primarily a measure of the ability of a species to stabilize a neighboring dipole by virtue of its own dipolarity and secondarily by its polarizability^{20,21}. It is a relative scale defined as π^* or π_2^* (cyclohexane = 0) and π^* or π_2^* (dimethyl sulfoxide = 1.00). Because aliphatic, aromatic and polyhalogenated species have very different polarizabilities it is often necessary to apply a “polarizability correction factor” (δ) to π^* or π_2^* (ref. 22). The δ parameter is conveniently defined to be 0 for aliphatics, 0.5 for polyhalogenated and 1.0 for aromatic species, whether it acts as a solvent or a solute. The α (α_2) and β (β_2) scales define the ability of a species to interact with an acceptor and a donor, respectively, via hydrogen bond formation^{21,23,24}. The above are referred to as solvatochromic parameters because in general they were first established via the study of some spectroscopic property of an appropriate indicator molecule^{22–24} in a variety of solvents. The solute hydrogen bond acidity and basicity parameters have been obtained by hydrogen bond complexation constants as well^{25,26}. These parameters have been used to correlate, rationalize and explore the chemistry of more than 600 different chemical systems^{21,27–29}. Studies of immediate relevance to this work include retention in reversed-^{30–34} and normal-phase liquid chromatography³⁵ and gas–liquid partition coefficients in both low-molecular-weight and polymeric liquids^{36–38}. In an early solvatochromic study Brady *et al.*³⁹

measured the bulk phase π^* of a series of methyl and phenyl silicone oils and showed that, after correction for the configurational entropy, excellent linear correlations for the residual free energy of transfer of polar solutes from liquid to gas phase against π^* were obtained.

In this work we measured the retention of 53 solutes on 8 different polymeric phases. In a sense this approach is similar to that taken by Rohrschneider and McReynolds in their use of probe solutes. However, it markedly differs from their methodology in that a large number of polar, hydrogen bond donor and hydrogen bond acceptor solutes were used. More importantly the test solutes were chosen to span an extremely wide range in chemical characteristics. In comparison to Rohrschneider we included such extremely strong hydrogen bond donor acids as trifluoroethanol ($\alpha_2 = 0.57$) and phenol ($\alpha_2 = 0.60$) and bases as strong as dimethyl sulfoxide ($\beta_2 = 0.78$) and dimethylacetamide ($\beta_2 = 0.74$). These are considerably stronger than the strongest acids and bases used by Rohrschneider (ethanol, dioxane, methyl ethyl ketone). Our solutes encompass nearly the entire range in available dipolarity (π_2^*), hydrogen bond acidity (α_2) and hydrogen bond basicity (β_2). At the same time we were interested in the behavior within a series of homologues, so we included several members of each class. This expands the solutes set to over the 30 or so compounds needed to precisely characterize a phase by regression methods. In principle, the coefficients of any regression model can be numerically determined as soon as one has as many data points as parameters in the model. Thus we really only need data for a handful of solutes. However, we deem this approach to be chemically unacceptable. First in order for the regression coefficients to be precisely defined each parameter should be varied over a reasonably wide range. Second the explanatory variables are imprecise since in general they are obtained by measurement. In order to average out the effect of this imprecision it is necessary to use a minimum of three to four solutes per parameter. We choose to vastly over-determine the system so as to generate a high degree of statistical and chemical confidence in the meaning of the parameters. As shown in Table I, this is an extremely diverse, variegated data set. In accord with the general LSER formalism for a study in which the solute is varied while the solvent environment is fixed the appropriate LSER regression equation is:

$$SP = SP_0 + mV_1/100 + s\pi_2^* + d\delta_2 + a\alpha_2 + b\beta_2 \quad (1)$$

SP is some solute property linearly related to its energy of solvation. In chromatography, it may be taken as the logarithm of the capacity factor ($\log k'$). SP_0 is a solute independent constant. m , s , a , b and d are regression coefficients. V_1 in eqn. 1 is the solute intrinsic (Van der Waals) molar volume (the same as the solvent value), computer calculated by the method of Leahy⁴⁶ or Pearlman⁴⁷, or estimated by simple additivity methods such as those of Bondi⁴⁸ or Abraham and McGowan⁴⁹. The $mV_1/100$ term is needed to account for the endoergic (unfavorable) energy of cavity formation. A scale of 1/100 for V_1 was used so that the parameter measuring the cavity term will cover roughly the same range as the other independent variables. This also makes it easier to evaluate the relative contributions of the various solute-solvent interactions to the property (SP) being studied.

When a very cohesive liquid, such as water, is used as the mobile phase the coefficient m should be large and positive leading to an increase in retention in

TABLE I
SOLUTE SOLVATOCHROMIC PARAMETERS

Compound name	$\log L^{16a}$	$V_{11}/100^d$	$\pi_2^*^d$	δ_2	β_2^e	α_2^e
Cyclohexane	2.913	0.598	0.00	0.0	0.00	0.00
1-Hexene	2.547	0.624	0.08	0.0	0.07	0.00
Pentane	2.162	0.553	-0.08	0.0	0.00	0.00
Hexane	2.668	0.648	-0.04	0.0	0.00	0.00
Octane	3.677	0.842	0.01	0.0	0.00	0.00
Decane	4.686	1.036	0.03	0.0	0.00	0.00
Undecane	5.191	1.134	0.04	0.0	0.00	0.00
Tetradecane	6.705	1.423	0.07	0.0	0.00	0.00
Pentadecane	7.209	1.521	0.07	0.0	0.00	0.00
Ethyl acetate	2.376	0.521	0.55	0.0	0.45	0.00
Propyl acetate	2.878	0.622	0.53	0.0	0.45	0.00
Diethyl ether	2.061	0.505	0.27	0.0	0.45 ^f	0.00
Dipropyl ether	2.989	0.699	0.27	0.0	0.46	0.00
Dibutyl ether	4.001	0.893	0.24	0.0	0.46	0.00
Acetonitrile	1.560	0.271	0.75	0.0	0.42 ^g	0.09
Propionitrile	1.940	0.369	0.70	0.0	0.43 ^g	0.00
Acetone	1.760	0.380	0.71	0.0	0.50 ^f	0.04
2-Butanone	2.287	0.477	0.67	0.0	0.48	0.03
2-Pentanone	2.755	0.574	0.65	0.0	0.48	0.03
Dimethylformamide	3.173	0.444	0.88	0.0	0.66 ^f	0.00
Dimethylacetamide	3.717	0.543	0.88	0.0	0.74 ^g	0.00
Dimethyl sulfoxide	3.437	0.466	1.00	0.0	0.78 ^f	0.00
Propionaldehyde	1.815	0.381	0.65	0.0	0.41	0.00
Tetrahydrofuran	2.534	0.455	0.58	0.0	0.51	0.00
Triethylamine	3.077	0.704	0.14	0.0	0.67 ^f	0.00
Nitromethane	1.892	0.348	0.85	0.0	0.25	0.12 ^g
Nitroethane	2.367	0.455	0.80	0.0	0.25	0.00
Nitropropane	2.710	0.542	0.78	0.0	0.25	0.00
Methanol	0.922	0.205	0.40	0.0	0.41 ^h	0.37 ⁱ
Ethanol	1.485	0.305	0.40	0.0	0.44 ^h	0.33 ⁱ
1-Propanol	2.097	0.402	0.40	0.0	0.45 ^h	0.33 ⁱ
2-Propanol	1.821	0.401	0.40	0.0	0.47 ^h	0.32 ⁱ
2-Methyl-2-propanol	2.018	0.498	0.40	0.0	0.49 ^h	0.32 ⁱ
Trifluoroethanol	1.224	0.376	0.73	0.0	0.18 ^h	0.57 ⁱ
Hexafluoroisopropanol	1.392	0.546	0.65	0.0	0.03 ^h	0.77 ⁱ
Acetic acid	1.750 ^b	0.323	0.60	0.0	0.45	0.55 ⁱ
Aniline	3.993	0.562	0.73	1.0	0.50	0.26
N-Methylaniline	4.492 ^c	0.660	0.73	1.0	0.47	0.12
Phenol	3.856	0.536	0.72	1.0	0.33	0.60 ⁱ
Benzyl alcohol	4.443	0.634	0.99	1.0	0.42 ^h	0.39
<i>m</i> -Cresol	4.329	0.634	0.68	1.0	0.34	0.58
Ethylamine	1.677	0.335	0.32	0.0	0.70	0.00
Propylamine	2.141	0.433	0.31	0.0	0.69	0.00
Butylamine	2.618	0.535	0.31	0.0	0.69	0.00
Benzene	2.803	0.491	0.59	1.0	0.13 ^g	0.00
Toluene	3.344	0.592	0.55	1.0	0.14 ^g	0.00
Ethylbenzene	3.765	0.668	0.53	1.0	0.12	0.00
Propylbenzene	4.221	0.769	0.51	1.0	0.12	0.00
<i>p</i> -Xylene	3.858	0.668	0.51	1.0	0.12	0.00
Benzaldehyde	3.935 ^c	0.606	0.92	1.0	0.44	0.00
Benzonitrile	3.913 ^c	0.590	0.90	1.0	0.37	0.00
N,N-Dimethylaniline	4.754	0.752	0.90	1.0	0.43	0.00
Carbon tetrachloride	2.823	0.514	0.28	0.5	0.10	0.00

^a From ref. 40 unless otherwise indicated. ^b From ref. 41. ^c From ref. 42. ^d From refs. 21 and 43. ^e From refs. 21 and 43 unless otherwise indicated. ^f From ref. 45. ^g These are β_2^H values provided to us by Professor R. W. Taft, University of California, Irvine, CA. ^h These are β_2^H values from ref. 44. ⁱ From ref. 25.

a non-polar stationary phase upon an increase in solute size. Such was invariably the case in studies of reversed-phase liquid chromatography^{31,33}. Abraham and co-workers^{50,51} in a study of gas partition coefficients into several non-polar liquids showed that eqn. 1 did not provide an acceptable correlation. This is due in part to the fact that in studies of liquid-liquid transfer processes the energy of dispersion between the solute and the two bulk liquid phases are to a first approximation similar and largely cancel out. This cancellation cannot occur in a gas to liquid or gas to solid transfer process. Eqn. 1 does not contain any explicit dependence on the energy of dispersion although it can be shown for a wide range of solutes that there is a high degree of covariance between molar refractivity (MR) (a dispersion interaction parameter) and V_1 (ref. 50). In addition detailed studies of the thermodynamics of retention in gas chromatography make it clear that there is a significant configurational entropy contribution to k' . Solvatochromic LSER regressions do not, at present, explicitly include a configurational entropy term but it too is expected to covary with V_1 .

Another distinction between liquid-liquid transfer and gas-condensed phase transfer processes is the fact that the free energy of transfer of a gas to water becomes less favorable as the gas increases in size whereas in all common organic liquids the free energy of transfer becomes more favorable, that is retention increases, as the size of the gas increases^{27,51}. This comes about due to the trade-off in increasingly unfavorable cavity formation and favorable dispersion energy with solute size.

Each of the solvatochromic coefficients (s , a and b) in eqn. 1 has a distinct chemical interpretation. On a phase that has no hydrogen bond donor acidity, e.g. hexadecane or squalane, a solute's hydrogen bond acidity and basicity should have no effect on its retention in which instance the a and b coefficients should be zero or statistically negligible. In contrast if the stationary phase were to have an active hydrogen bond donor group, such as a hydroxyl group, then one expects the b coefficient of this material to be positive. That is, an increase in solute basicity should lead to an increase in retention. By the same concept, for a highly dipolar but hydrogen bond donor inert phase one expects the s coefficient to be significant and an increase in solute dipolarity should lead to an increase in retention.

To overcome the problems inherent in eqn. 1 Abraham and co-workers^{27,51} have recommended that a new solute parameter $\log L^{16}$ be used to replace V_1 in eqn. 1 when dealing with gas-condensed phase processes.

$$SP = SP_0 + l \log L^{16} + s\pi_2^* + d\delta_2 + a\alpha_2 + b\beta_2 \quad (2)$$

L^{16} is the partition coefficient of the solute from the gas phase to *n*-hexadecane at 298 K. It takes into account both solute-condensed phase dispersion interactions and the work needed to create a cavity in the condensed phase. They have shown that this provides much better correlations for gas-liquid transfer processes than does eqn. 1. A similar approach was taken in this work. The initial motivation for this work was to explore the utility of the LSER given in eqn. 2 and ultimately to classify a variety of capillary columns and at the same time to see if their chemical properties as defined by the coefficients l , s , a and b could be rationalized.

EXPERIMENTAL

Unless otherwise stated, all solutes were general laboratory or analytical grade in the highest purity available. The capillary columns, which span the whole polarity scale (not including DB-23), were all a gift from J&W Scientific (Folsom, CA, U.S.A.). Their specifications and chemical structures are given in Table II. All columns used here were 15-m widebore columns. An HP-7620A gas chromatograph with heated on-column injector and flame ionization detector were used. Both the injector and the detector temperatures were kept at 250°C. Data were collected at 45, 60, 80, 115 and 150°C. The column oven temperature was stable to within 0.02°C. Helium (carrier gas) flow was adjusted as necessary to make the retention times adequate. The samples were injected either as headspace vapors (for liquid solutes) or as very dilute solutions of the solids. Sample sizes were varied to insure that the retention times were independent of the amount injected. All data were collected on an HP-3390 integrator. Corrected retention times and capacity factors were calculated referenced to the retention of methane. Data were analyzed via a multivariable linear least square regression program run on a Zenith computer.

TABLE II

PROPERTIES OF THE CAPILLARY COLUMNS USED IN THE STUDY

The polarity increases from columns 1 to 8.

<i>Megabore column</i>	<i>Phase</i>	<i>Film thickness (μm)</i>
1 DB-1	Methylsilicone	1.5
2 DB-5	5% Phenyl methylsilicone	1.5
3 DB-1301	6% Cyanopropylphenyl methylsilicone	1.0
4 DB-1701	14% Cyanopropylphenyl methylsilicone	1.0
5 DB-17	50% Phenyl methylsilicone	1.0
6 DB-210	50% Trifluoropropyl methylsilicone	1.0
7 DB-225	50% Cyanopropylphenyl methylsilicone	1.0
8 DB-WAX	Polyethylene glycol	1.0

RESULTS AND DISCUSSION

The results of preliminary correlations using eqn. 1 for eight different columns are shown in Table III. For brevity the results are given only at 115°C. The standard deviations and correlation coefficients shown in Table III when compared to those obtained in related studies, particularly reversed-phase liquid chromatography, indicate that these correlations are very imprecise. This is especially true of the more polar stationary phases. The correlations for the DB-WAX column are particularly poor (see below).

Even though the correlations are not as precise as we desire or can ultimately achieve (see below) the various solvatochromic coefficients m , s , a , b and d are statistically significant and should be interpreted. The coefficients m , s , b and d are

TABLE III
REGRESSION COEFFICIENTS BASED ON V_1 AND SOLVATOCHROMIC PARAMETERS

Standard deviations of the coefficients are given in parentheses. Eqn. 1 is the regression equation employed.

Column	$T(^{\circ}\text{C})$	SP_0	m	s	a	b	d	$S.D.^a$	r^b	n^c	f^d
DB-1	115	-2.41 (0.11)	2.60 (0.12)	0.47 (0.11)	- ^e	0.46 (0.13)	0.51 (0.07)	0.17	0.9677	53	0.22
DB-5	115	-2.54 (0.12)	2.64 (0.13)	0.63 (0.13)	- ^e	0.44 (0.15)	0.49 (0.07)	0.19	0.9617	53	0.23
DB-1301	115	-2.78 (0.14)	2.69 (0.15)	0.89 (0.14)	0.31 (0.15)	0.42 (0.16)	0.44 (0.08)	0.21	0.9575	52 ^f	0.24
DB-1701	115	-2.76 (0.14)	2.59 (0.15)	1.13 (0.14)	0.50 (0.16)	0.37 (0.17)	0.40 (0.08)	0.21	0.9537	53	0.26
DB-17	115	-2.88 (0.16)	2.57 (0.18)	1.03 (0.17)	- ^e	0.60 (0.20)	0.59 (0.10)	0.26	0.9390	52 ^f	0.28
DB-210	115	-2.79 (0.15)	2.14 (0.16)	1.51 (0.15)	- ^e	0.54 (0.18)	0.18 (0.09)	0.23	0.9296	53	0.28
DB-225	115	-2.90 (0.17)	2.30 (0.18)	1.72 (0.17)	0.79 (0.19)	0.49 (0.21)	0.42 (0.10)	0.26	0.9400	53	0.31
DB-WAX	115	-2.83 (0.20)	2.11 (0.22)	1.73 (0.20)	1.79 (0.23)	0.64 (0.24)	0.55 (0.12)	0.31	0.9371	53	0.34

^a Standard deviation of the fit.

^b Correlation coefficient.

^c Number of data points.

^d Goodness-of-fit statistic⁵².

^e These coefficients were found to be not significantly different from zero and were omitted in the final fit.

^f Propionaldehyde was excluded from DB-1301 data sets, acetic acid was excluded from DB-17, due to their being outliers at all temperatures on the respective column.

significant on all phases. The coefficients a is insignificant on four phases. The signs and magnitudes of s make chemical sense. In general s increases as the phase becomes more polar. This means that solute dipolarity causes a greater increase in retention on a more dipolar phase. The m coefficient first increases then decreases as the phase becomes more polar. This can be rationalized by viewing m as being the result of dispersive and inductive solute-solvent interactions, the configurational entropy and the cavity formation processes in the solvent. The a coefficients for the DB-1, DB-5, DB-17 and DB-210 columns are not significant. The functional groups in these phases are known to be very weak acceptors of hydrogen bonds based on their effect on the spectra of Kamlet-Taft indicators that are able to donate hydrogen bonds⁵³. However, the standard deviations of the fit are too large to let us see the low basicity of these phases. In contrast, 3-cyanopropylphenyl methylsilicone has a significant basicity [$\beta(\text{propyl cyanide}) = 0.43$], thus the a coefficients for the three cyano phases (DB-1301, DB-1701 and DB-225) are significant and as expected increase as the percentage of the 3-cyanopropyl group increases. DB-WAX is both the most acidic [$\alpha(\text{ethylene glycol}) = 0.90$] and basic [$\beta(\text{ethylene glycol}) = 0.52$] phase studied so its a and b coefficients are the largest. These coefficients agree well with the qualitative basicity, acidity, polarity and London potential of the similar phases given by Chong *et al.*⁵⁴. Thus despite the overall poor precision of these fits all the coefficients can be rationalized.

TABLE IV
SUMMARY OF STANDARD DEVIATIONS OF THE FITS OBTAINED IN ALL STUDIES^a

All results pertain to 45°C except where noted.

Model	Column type									
	DB-1	DB-5	DB-1301	DB-1701	DB-17	DB-210	DB-225	DB-WAX	DB-WAX ^b	
V_1 + solvatochromic parameters ^a	0.24	0.25	0.26	0.28	0.34	0.30	0.34	0.41	0.37	
$\log L_{16}$ + solvatochromic parameters ^b	0.08	0.08	0.13	0.13	0.15	0.17	0.19	0.31	0.23	
$\log L_{16}$ + $\log k'_{DB-WAX,115^\circ C}$ ^c	0.08	0.08	0.12	0.13	0.18	0.33	0.13	0.15	0.09	
$\log k'_{DB-1,115^\circ C}$ + $\log k'_{DB-WAX,115^\circ C}$ ^d	0.11	0.09	0.15	0.15	0.16	0.32	0.12	0.15	0.09	
$\log L_{16}$ + $\log k'_{DB-WAX,115^\circ C}$ ^e	0.06	0.06	0.10	0.08	0.09	0.09	0.07	0.15	0.04	
+ solvatochromic parameters										
$\log k'_{DB-1,115^\circ C}$ + $\log k'_{DB-WAX,115^\circ C}$ ^f	0.08	0.07	0.11	0.09	0.07	0.09	0.06	0.13	0.04	
+ solvatochromic parameters										
$\log L_{16}$ + solvatochromic parameters ^b (115°C)	0.07	0.07	0.10	0.10	0.12	0.13	0.15	0.22	0.20	
$\log L_{16}$ + solvatochromic parameters ^b (80°C)	0.06	0.08	0.10	0.11	0.13	0.14	0.17	0.25	0.22	
$\log L_{16}$ + solvatochromic parameters ^b (25°C)	0.10	0.09	0.16	0.15	0.16	0.18	0.21	0.37	0.24	

^a Data were regressed against eqn. 1.

^b Data were regressed against eqn. 2.

^c Data were regressed against eqn. 3.

^d Data were regressed against eqn. 4.

^e Data were regressed against eqn. 5.

^f Data were regressed against eqn. 6.

^g Amines were excluded from the data sets (see text).

TABLE V
REGRESSION COEFFICIENTS BASED ON $\log L^{16}$ AND SOLVATOCHROMIC PARAMETERS^a

Eqn. 2 is the regression equation employed. Standard deviations of the coefficients are given in parentheses.

Column	$T(^{\circ}\text{C})$	SP_0	l	s	a	b	d	S.D.	r	n	f	R^a	$R_{\text{crit.}}^b$
DB-1	115	-1.88 (0.03)	0.49 (0.01)	- ^c	- ^c	- ^c	0.13 (0.03)	0.07	0.9944	53	0.09	2.39	1.10
DB-5	115	-2.15 (0.03)	0.52 (0.01)	0.33 (0.03)	- ^c	- ^c	- ^c	0.07	0.9947	53	0.09	2.67	1.10
DB-1301	115	-2.37 (0.05)	0.53 (0.01)	0.52 (0.05)	0.47 (0.07)	- ^c	- ^c	0.10	0.9897	52	0.12	2.03	1.10
DB-1701	115	-2.37 (0.04)	0.51 (0.01)	0.75 (0.05)	0.66 (0.07)	- ^c	- ^c	0.10	0.9902	53	0.12	2.15	1.10
DB-17	115	-2.48 (0.06)	0.51 (0.02)	0.81 (0.07)	- ^c	- ^c	0.11 (0.05)	0.12	0.9860	52	0.14	2.06	1.07
DB-210	115	-2.41 (0.07)	0.42 (0.02)	1.36 (0.07)	-0.20 (0.10)	- ^c	-0.21 (0.05)	0.13	0.9777	53	0.16	1.76	1.14
DB-225	115	-2.58 (0.07)	0.46 (0.02)	1.48 (0.07)	0.93 (0.11)	- ^c	- ^c	0.15	0.9799	53	0.18	1.71	1.10
DB-WAX	115	-2.60 (0.10)	0.45 (0.02)	1.69 (0.10)	1.94 (0.16)	- ^c	- ^c	0.22	0.9679	53	0.25	1.39	1.10

^a Ratio of the f values in Table III and Table V.

^b $R_{\text{crit.}}$ was calculated by eqn. 5 or eqn. 6 in ref. 52 at a confidence level of 99%.

^c These coefficients were found to be not significantly different from zero and were omitted in the final fit.

What is most important to note is the nearly monotonic deterioration in the goodness of fit as measured by either the root mean square residual (S.D.) or the correlation coefficient (r) as the phase polarity increases (see Table III). Because we will compare various models and data sets in terms of the overall standard deviations all of the important comparisons are compiled in Table IV for easy reference. In comparing the various models only the worst case results at the extreme temperature (45°C) are given in Table IV. The results at other temperatures using eqn. 2 are also given in this table.

As expected, based on the work of Abraham and co-workers^{27,51}, all correlations improved significantly when $\log L^{16}$ was used in place of V_1 (see F test⁵² in Table V). In all cases, the f ratio R is greater than $R_{crit.}$. In fact for the non-polar phases (the DB-1 and DB-5 columns) quite acceptable correlations *versus* $\log L^{16}$ were obtained. The regression coefficients (s , a and b) of the solvatochromic parameters are slightly different when eqn. 2 is used compared to eqn. 1. First, the b coefficient is insignificant for all phases, and not all of the d coefficients are significant. The l , s and a coefficients make chemical sense for the same reasons as stated for the V_1 regression (eqn. 1), with the exception of the small negative a coefficient for DB-210. We also note (see Tables IV and V) that the fit quality still decreases as the phase polarity increases. Again we want to point out that the DB-WAX column gave particularly poor results. A detailed examination of the data set for this column showed that a large part of the variance for the DB-WAX phase at lower temperatures was due to the amine solutes. We note here that the amines gave very respectable peak shapes on all the other columns at all temperatures but they gave broad tailed peaks on the DB-WAX column at low temperatures. It is quite possible that the peak maximum is not a good measure of retention under these conditions and consequently the data for the amines may be invalid. However, we did not want to bias the results by deleting them from the analysis. When we do so the S.D. values for the DB-WAX phase drop to the level of the other phases as shown in the last column in Table IV.

There are two distinct categories of explanations for the lack of fit. First, our experimental k' values might be imprecise. Second, the model itself might be wrong and/or the parameters inaccurate. The lack of fit exhibited in the above sets of data is definitely not due to random experimental errors in the measurements of k' . If all or most of the variance in the fits were due to random errors in the measurement of the k' values then fits of $\log k'$ to $1/T$ (Van 't Hoff plots) should be only marginally better than fits to any model dependent correlations such as eqns. 1 and 2. In fact we examined plots of $\log k'$ vs. $1/T$ for each solute on each column and invariably obtained very good straight lines. The S.D. values for fits of $\log k'$ vs. $1/T$ for a single compound ranged from as low as 0.005 to in some cases as high as 0.04. Typically the S.D. values for this type of fit were about 0.02. These are far better than any of the results reported for regressions of $\log k'$ vs. either model equation. We are convinced that the average standard deviations reported in Tables III, IV and V are not due to the experimental precision in the measurement of $\log k'$.

One possible source of model error in this study, not previously encountered in other linear solvation energy studies, is that the data (k' values) were not obtained at 25°C. We note that the solvatochromic parameters π^* , α and β are generally measured at room temperature and they are known to be at least somewhat temperature dependent^{55,56}. The results given in Table IV indicate that, if anything, the fits at 45°C

are worse than the fits at higher temperatures. Thus we felt this explanation to be unlikely. This was confirmed by using the above-mentioned Van 't Hoff plots to extrapolate the $\log k'$ values to 25°C. These data were then regressed vs. eqn. 2. As shown in Table IV the average standard deviations at 25°C are, if anything, worse than those at higher temperatures. We must conclude that either eqn. 2 is an invalid model of retention or that the parameters are incorrect.

At this point we want to emphasize a purely empirical but very useful observation. We tested a "double" linear regression model⁵⁷, that is, retention data on two extremely different columns were used as the explanatory variables. The regression equations tested were:

$$\log k'(T) = SP_0 + l \log k'_{\text{DB-1},115^\circ\text{C}} + w \log k'_{\text{DB-WAX},115^\circ\text{C}} \quad (3)$$

$$\log k'(T) = SP_0 + l \log L^{16} + w \log k'_{\text{DB-WAX},115^\circ\text{C}} \quad (4)$$

where $k'_{\text{DB-1},115^\circ\text{C}}$ and $k'_{\text{DB-WAX},115^\circ\text{C}}$ denote the capacity factors on the DB-1 and DB-WAX columns obtained at a temperature of 115°C.

Refer to Table IV for a comparison to the preceding regressions. As expected there were improvements in the fits for the polar phases, but not for the phases of intermediate and low polarity. For the non-polar phase, either $\log L^{16}$ or the retention on DB-1 give about the same results. The F test shows that $\log L^{16}$ is slightly better than DB-1 for 4 data sets. Use of just the double regression cannot explain all the data, that is, the average S.D. is not yet at 0.02.

Finally we added the solvatochromic parameters as additional explanatory variables (eqns. 5 and 6).

$$\log k' = SP_0 + l \log L^{16} + w \log k'_{\text{DB-WAX},115^\circ\text{C}} + s\pi_2^* + d\delta_2 + a\alpha_2 + b\beta_2 \quad (5)$$

$$\log k' = SP_0 + l \log k'_{\text{DB-1},115^\circ\text{C}} + w \log k'_{\text{DB-WAX},115^\circ\text{C}} + s\pi_2^* + d\delta_2 + a\alpha_2 + b\beta_2 \quad (6)$$

The results are given in Tables VI and VII. Again see Table IV for a summary. Clearly the use of retention on two extremely different types of columns in addition to the solvatochromic parameters as explanatory variables significantly improved the goodness of fit. The average standard deviations for all the columns are now considerably better than in any of the preceding fits although they still exceed 0.02, which we feel represents the level of exhaustive fitting, as obtained in fits of $\log k'$ to $1/T$. In any case the fits are now as good as those observed in previous studies of liquid chromatography.

The improvement in the fits is purely statistical. By using retention on two extreme types of columns we have weakened the dependence of $\log k'$ on all of the solvatochromic parameters. That is, the fitting coefficients s , a and b in eqns. 5 and 6 are a good deal smaller than those in eqns. 1 and 2. Consequently the values of π_2^* , α_2 and β_2 , and therefore errors in these parameters, now have less influence on the computed $\log k'$ values. Obviously experimental imprecision in the measured retentions on the DB-1 and the DB-WAX columns will be reflected in the precision of the computed $\log k'$ values.

The above is admittedly a highly empirical approach in that retention on the

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Eqn. 5 is the regression equation employed. Standard deviations of the coefficients are given in parentheses.

Column	T(°C)	Int.	l	w	s	a	b	d	S.D.	r	n	f
DB-1	150	-2.07 (0.03)	0.43 (0.01)	- ^a	- ^a	- ^a	- ^a	0.15 (0.03)	0.09	0.9898	53	0.09
	115	-1.81 (0.02)	0.47 (0.01)	0.07 (0.01)	- ^a	- ^a	- ^a	0.07 (0.02)	0.06	0.9967	53	0.07
	80	-1.56 (0.03)	0.55 (0.01)	0.15 (0.01)	- ^a	- ^a	-0.11 (0.03)	- ^a	0.05	0.9980	53	0.06
	45	-1.28 (0.04)	0.66 (0.01)	0.22 (0.02)	- ^a	- ^a	-0.21 (0.04)	-0.11 (0.03)	0.06	0.9980	53	0.05
DB-5	150	-1.76 (0.04)	0.37 (0.01)	0.18 (0.02)	- ^a	-0.34 (0.06)	- ^a	- ^a	0.06	0.9942	53	0.07
	115	-1.53 (0.05)	0.41 (0.01)	0.22 (0.02)	- ^a	-0.44 (0.06)	-0.12 (0.04)	- ^a	0.05	0.9971	53	0.07
	80	-1.43 (0.05)	0.51 (0.01)	0.22 (0.02)	- ^a	-0.21 (0.06)	-0.13 (0.04)	- ^a	0.05	0.9978	53	0.07
	45	-1.32 (0.04)	0.64 (0.01)	0.24 (0.02)	- ^a	- ^a	-0.16 (0.05)	-0.09 (0.03)	0.07	0.9978	53	0.06
DB-1301	115	-1.64 (0.03)	0.40 (0.01)	0.28 (0.02)	- ^a	- ^a	- ^a	- ^a	0.08	0.9935	52	0.09
	80	-1.23 (0.04)	0.45 (0.01)	0.38 (0.02)	- ^a	- ^a	-0.13 (0.05)	-0.09 (0.03)	0.07	0.9968	52	0.08
	60	-0.96 (0.05)	0.49 (0.01)	0.46 (0.02)	- ^a	- ^a	-0.18 (0.06)	-0.16 (0.03)	0.08	0.9959	52	0.08
	45	-0.77 (0.06)	0.52 (0.01)	0.52 (0.02)	- ^a	- ^a	-0.22 (0.07)	-0.20 (0.04)	0.10	0.9949	52	0.08
DB-1701	150	-1.40 (0.09)	0.26 (0.01)	0.39 (0.03)	0.12 (0.05)	-0.34 (0.07)	-0.23 (0.04)	-0.07 (0.02)	0.04	0.9973	53	0.04
	115	-1.31 (0.08)	0.33 (0.01)	0.41 (0.03)	0.20 (0.05)	-0.14 (0.07)	-0.19 (0.03)	-0.11 (0.02)	0.05	0.9981	53	0.05
	80	-1.12 (0.05)	0.42 (0.01)	0.46 (0.02)	0.26 (0.05)	- ^a	-0.23 (0.05)	-0.18 (0.03)	0.06	0.9973	53	0.07
	60	-0.82 (0.07)	0.45 (0.01)	0.55 (0.03)	0.19 (0.07)	- ^a	-0.26 (0.06)	-0.22 (0.03)	0.07	0.9967	53	0.07
45	-0.89 (0.16)	0.53 (0.03)	0.50 (0.06)	0.35 (0.10)	0.29 (0.13)	-0.30 (0.07)	-0.27 (0.04)	0.08	0.9966	53	0.07	

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DB-17	150	-1.44 (0.05)	0.25 (0.01)	0.42 (0.03)	- ^a	-0.89 (0.09)	- ^a	0.08 (0.04)	0.09	0.9905	52	0.08
	115	-1.18 (0.05)	0.29 (0.01)	0.52 (0.02)	- ^a	-0.98 (0.08)	- ^a	- ^a	0.08	0.9940	52	0.09
	80	-0.91 (0.05)	0.35 (0.01)	0.59 (0.02)	- ^a	-1.03 (0.08)	- ^a	- ^a	0.08	0.9953	52	0.10
	45	-0.91 (0.17)	0.48 (0.03)	0.56 (0.06)	0.24 (0.11)	-0.85 (0.13)	- ^a	- ^a	0.09	0.9961	52	0.08
DB-210	115	-1.09 (0.13)	0.19 (0.02)	0.52 (0.05)	0.52 (0.09)	-1.19 (0.10)	- ^a	-0.27 (0.03)	0.07	0.9937	53	0.08
	80	-0.87 (0.13)	0.25 (0.02)	0.58 (0.05)	0.62 (0.09)	-1.24 (0.11)	- ^a	-0.34 (0.03)	0.07	0.9950	53	0.10
	60	-0.77 (0.15)	0.30 (0.03)	0.61 (0.06)	0.71 (0.10)	-1.22 (0.12)	- ^a	-0.39 (0.03)	0.08	0.9949	53	0.10
	45	-0.64 (0.16)	0.34 (0.03)	0.65 (0.06)	0.78 (0.11)	-1.24 (0.14)	- ^a	-0.43 (0.04)	0.09	0.9948	53	0.09
DB-225	150	-0.95 (0.13)	0.10 (0.02)	0.66 (0.05)	0.36 (0.08)	-0.51 (0.11)	-0.18 (0.06)	-0.07 (0.03)	0.07	0.9948	53	0.07
	115	-0.96 (0.11)	0.19 (0.02)	0.64 (0.04)	0.45 (0.07)	-0.29 (0.09)	- ^a	-0.08 (0.03)	0.06	0.9967	53	0.07
	80	-0.80 (0.06)	0.27 (0.01)	0.68 (0.02)	0.57 (0.05)	- ^a	- ^a	-0.12 (0.03)	0.06	0.9974	53	0.07
	45	-0.26 (0.06)	0.31 (0.01)	0.84 (0.02)	0.53 (0.05)	- ^a	- ^a	-0.19 (0.03)	0.07	0.9979	53	0.05
DB-WAX	80	0.48 (0.02)	- ^a	1.16 (0.02)	- ^a	- ^a	0.10 (0.05)	- ^a	0.07	0.9962	49	0.08
	60	0.88 (0.02)	- ^a	1.29 (0.03)	- ^a	- ^a	- ^a	- ^a	0.12	0.9891	45	0.13
	45	1.19 (0.03)	- ^a	1.39 (0.04)	- ^a	- ^a	- ^a	- ^a	0.15	0.9836	45	0.14

^a These coefficients were found to be not significantly different from zero and were omitted in the final fit.

TABLE VII
 FINAL MULTIPLE REGRESSION RESULTS WITH DUAL-COLUMN RETENTION AND SOLVATOCROMIC PARAMETERS
 Eqn. 6 is the regression equation employed. Standard deviations of the coefficients are given in parentheses.

Column	T(°C)	Int.	l	w	s	a	b	d	S.D.	r	n	f
DB-1	150	-0.41 (0.01)	0.89 (0.01)	- ^a	- ^a	- ^a	- ^a	- ^a	0.06	0.9953	53	0.06
	80	0.48 (0.01)	1.17 (0.02)	0.03 (0.01)	- ^a	- ^a	- ^a	- ^a	0.06	0.9970	53	0.08
	45	1.23 (0.03)	1.37 (0.02)	0.12 (0.02)	- ^a	- ^a	-0.23 (0.06)	-0.20 (0.03)	0.08	0.9967	53	0.07
DB-5	150	-0.37 (0.01)	0.79 (0.02)	0.09 (0.02)	- ^a	-0.26 (0.06)	- ^a	- ^a	0.06	0.9952	53	0.06
	115	-0.02 (0.01)	0.92 (0.02)	0.10 (0.01)	- ^a	-0.28 (0.05)	- ^a	- ^a	0.05	0.9977	53	0.06
	80	0.42 (0.01)	1.12 (0.02)	0.07 (0.01)	- ^a	- ^a	- ^a	- ^a	0.07	0.9966	53	0.08
DB-1301	45	1.07 (0.02)	1.37 (0.02)	0.12 (0.02)	- ^a	- ^a	- ^a	-0.16 (0.03)	0.08	0.9970	53	0.07
	115	-0.13 (0.01)	0.84 (0.02)	0.21 (0.02)	- ^a	- ^a	- ^a	- ^a	0.08	0.9935	52	0.09
	80	0.39 (0.02)	0.99 (0.03)	0.23 (0.03)	- ^a	0.16 (0.09)	- ^a	- ^a	0.09	0.9938	52	0.11
DB-1701	60	0.81 (0.02)	1.09 (0.03)	0.32 (0.03)	- ^a	0.19 (0.10)	- ^a	-0.20 (0.04)	0.10	0.9943	52	0.10
	45	1.22 (0.04)	1.09 (0.03)	0.44 (0.03)	- ^a	- ^a	-0.23 (0.08)	-0.27 (0.05)	0.11	0.9932	52	0.10
	150	-0.36 (0.01)	0.50 (0.02)	0.40 (0.01)	- ^a	-0.39 (0.04)	-0.20 (0.03)	-0.09 (0.02)	0.04	0.9981	53	0.04
DB-1701	115	0.04 (0.02)	0.62 (0.02)	0.45 (0.02)	- ^a	-0.26 (0.06)	-0.17 (0.04)	-0.14 (0.02)	0.05	0.9975	53	0.06
	80	0.56 (0.02)	0.81 (0.02)	0.47 (0.02)	- ^a	- ^a	-0.15 (0.05)	-0.20 (0.03)	0.07	0.9962	53	0.09
	60	0.94 (0.02)	0.89 (0.02)	0.54 (0.02)	- ^a	- ^a	-0.20 (0.05)	-0.25 (0.03)	0.08	0.9963	53	0.08
45	1.29 (0.03)	0.95 (0.03)	0.60 (0.02)	- ^a	- ^a	-0.28 (0.06)	-0.32 (0.04)	0.09	0.9955	53	0.08	

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DB-17	150	-0.49 (0.01)	0.53 (0.03)	0.39 (0.02)	- ^a	-0.87 (0.09)	- ^a	- ^a	0.09	0.9907	52	0.08
	115	-0.09 (0.01)	0.62 (0.02)	0.45 (0.02)	- ^a	-0.92 (0.07)	- ^a	- ^a	0.07	0.9951	52	0.08
	80	0.39 (0.01)	0.75 (0.02)	0.50 (0.02)	- ^a	-0.96 (0.07)	- ^a	- ^a	0.07	0.9964	52	0.08
	45	1.03 (0.01)	0.92 (0.03)	0.58 (0.02)	- ^a	-0.98 (0.08)	- ^a	- ^a	0.08	0.9967	52	0.07
DB-210	115	-0.38 (0.04)	0.42 (0.04)	0.47 (0.05)	0.54 (0.08)	-1.13 (0.10)	- ^a	-0.29 (0.03)	0.07	0.9946	53	0.08
	80	0.09 (0.05)	0.55 (0.05)	0.53 (0.05)	0.62 (0.09)	-1.18 (0.11)	- ^a	-0.37 (0.03)	0.07	0.9955	53	0.09
	60	0.38 (0.05)	0.66 (0.05)	0.55 (0.06)	0.72 (0.09)	-1.15 (0.12)	- ^a	-0.43 (0.03)	0.08	0.9956	53	0.09
	45	0.66 (0.06)	0.74 (0.06)	0.58 (0.06)	0.79 (0.10)	-1.16 (0.13)	- ^a	-0.47 (0.04)	0.09	0.9955	53	0.08
DB-225	150	-0.65 (0.05)	0.27 (0.05)	0.57 (0.05)	0.34 (0.09)	-0.36 (0.11)	- ^a	- ^a	0.08	0.9936	53	0.08
	115	-0.26 (0.03)	0.42 (0.04)	0.59 (0.04)	0.48 (0.06)	-0.22 (0.08)	- ^a	-0.11 (0.02)	0.05	0.9976	53	0.06
	80	0.23 (0.02)	0.56 (0.02)	0.64 (0.02)	0.55 (0.04)	- ^a	- ^a	-0.16 (0.02)	0.05	0.9984	53	0.06
	45	0.94 (0.02)	0.64 (0.02)	0.80 (0.02)	0.50 (0.05)	- ^a	- ^a	-0.23 (0.02)	0.06	0.9984	53	0.04
DB-WAX	80	0.56 (0.03)	-0.05 (0.02)	1.24 (0.03)	-0.20 (0.06)	- ^a	0.16 (0.05)	- ^a	0.07	0.9969	49	0.08
	60	0.98 (0.05)	-0.10 (0.04)	1.43 (0.05)	-0.37 (0.10)	- ^a	0.23 (0.08)	- ^a	0.10	0.9927	45	0.11
	45	1.33 (0.06)	-0.14 (0.05)	1.58 (0.06)	-0.51 (0.12)	- ^a	0.32 (0.10)	- ^a	0.13	0.9895	45	0.11

^a These coefficients were found to be not significantly different from zero and were omitted in the final fit.

more polar reference column depends on and correlates with the solvatochromic parameters. The degree of covariance is not so high as to cause excessive variance inflation (see below) in the regression coefficients.

All of the results shown in Tables VI and VII are much more precise than the results given in Tables III and V. Before discussing the details of these results we should state that other pairs of "reference" columns were evaluated. There are no appreciable differences in the quality of the fits whether we use $\log L^{16}$ or the retention on DB-1. Since retention data on commercial permethyl silicone oil columns are easier to obtain than are data on hexadecane columns and for very polar solutes are less likely to show interfacial effects, we opted to use the data obtained with a DB-1 column instead of the $\log L^{16}$ data. Second, we found that the DB-WAX column was the best polar "reference" column. By this we mean that it gave good fits for all other types of columns while columns of intermediate polarity only served to correlate results for lesser and equally polar phases but failed to correlate the results for more polar columns. Thus the overall quality of the regression markedly improved as the polarity of the second reference column increased.

The above "double-reference" column empirical approach greatly complicates the chemical interpretation of the coefficients s , d , a and b in eqns. 5 and 6. This complication comes about because both the signs and the magnitude of these coefficients now have meaning only in relation to the nature of the reference columns. If retention on the non-polar reference column were utterly insensitive to solute hydrogen bond acidity and basicity then the observed a and b coefficients for eqns. 5 and 6 would depend only on the characteristics of the test column and the more polar reference column. However, s and d do vary between different non-polar references ($\log k'_{\text{DB-1, 115}^\circ\text{C}}$ and $\log L^{16}$), thus s and d will, in general, depend upon the properties of both reference columns.

Despite the chemical complications in interpreting the solvatochromic coefficients obtained when retention data are fit to equations such as 5 and 6, the approach does lead to an empirical scheme for precise classification of phases. Phases with similar chemical structures will have similar phase coefficients (l , w , s , d , a and b). When eqn. 6 is used the most important coefficients will be l and w . Phases which chemically resemble DB-1 will have a significant l coefficient and a small value for w , a and b . Similarly, a phase which is *identical* to the DB-WAX column will have a large w coefficient and statistically negligible values for l , s , d , a and b . For intermediate polarity phases, the l and w coefficients will lie between the above two extreme cases. Solute-stationary phase interactions different from those in DB-WAX will be reflected in the respective coefficients of the solvatochromic parameters.

In order to see how the solvatochromic regression method can be used to classify columns, consider the data plotted in Fig. 1. The column type is displayed on the x -axis and the two most important coefficients (l and w) are plotted on the y -axis. Note the "I" bars indicate the precision of the l and w coefficients. Only data for 45°C are shown in the figure. It is evident that the DB-1 and DB-5 columns are numerically very similar since both l and w are identical for both columns. This is hardly surprising since DB-1 and DB-5 are chemically very similar (see Table II). We also note that the DB-1701 and DB-17 columns have both l and w values which are statistically indistinguishable. Table II indicates that these two columns ought to be chemically distinct since the DB-1701 is a 14% cyanopropylphenyl methyl silicone oil and the DB-17 is a 50%

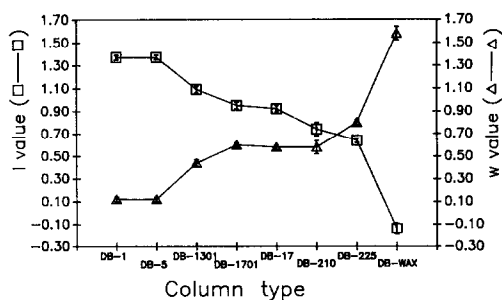


Fig. 1. Classification of columns according to l and w coefficients.

phenyl methylsilicone oil. A reviewer pointed out to us that 1701 type materials were introduced as alternatives to 17 type phases. Thus in retrospect it is interesting that such chemically different materials were classified as being so similar by our approach. However, this apparent failure to differentiate these two chemically distinct phases based on l and w is not real. Inspection of Fig. 2 which shows plots of s , a , b and d versus column type demonstrate that the DB-17 column has a very large negative a coefficient (-0.98) whereas the a value for the cyano phase is quite small, *i.e.* the basicity of the DB-1701 is much stronger than that of DB-17. In fact when all of the fitting coefficients are considered no two of these columns are seen to be chemically equivalent within the statistics of the fit. The discriminating power of the approach is related to the precision of the overall fits to the model equation. Thus any two phases whose coefficients differ by more than the indicated brackets are chemically distinct.

The effect of temperature on the two leading coefficients (l and w) is shown in Fig. 3 where results at 45, 80 and 115°C are shown. In this plot we use the two coordinates l and w to define a "phase plane". At a given temperature l and w are almost linearly related. We see the near coincidence of the DB-1 and DB-5 columns, and the DB-1701 and DB-17 columns at 45°C. At a higher temperature this similarity in terms of l and w for the pairs of columns no longer persists.

The present classification scheme is also useful in a predictive sense. Suppose that one wants to discriminate between two or more species which differ primarily in their hydrogen bond donor characteristics, the present method suggests the use of a column with the greatest overall dependence on w and a . The applicability of this idea will be explained in subsequent communications.

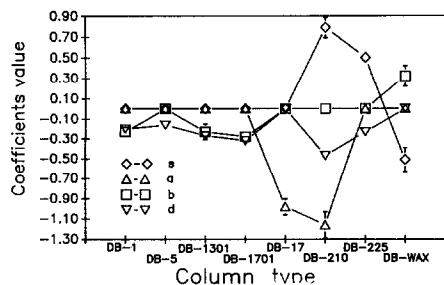


Fig. 2. Classification of columns according to solvatochromic parameter coefficients.

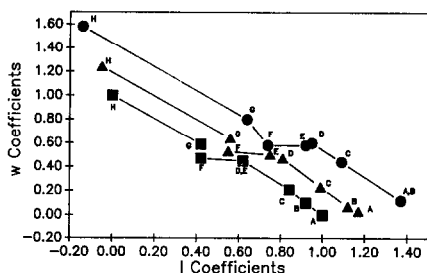


Fig. 3. Column polarity (l and w coefficients) vs. temperature. A = DB-1; B = DB-5; C = DB-1301; D = DB-1701; E = DB-17; F = DB-210; G = DB-225; H = DB-WAX. ● = 45°C; ▲ = 80°C; ■ = 115°C.

ACKNOWLEDGEMENT

This work was supported in part by grants to the University of Minnesota from the National Science Foundation and the Petroleum Research Foundation.

SUPPLEMENTARY MATERIAL AVAILABLE

All the log capacity factors are available either on a computer disk or on paper upon request.

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