Hydrogen Bonding. Part 13.† A New Method for the Characterisation of GLC Stationary Phases—The Laffort Data Set

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A number of equations for the correlation of retention data for a series of solutes on a given stationary phase (or solvent) have been investigated with the aim of characterising stationary phases. The two most successful equations are,

$$\mathrm{SP} = c + d\delta_2 + s\pi_2^* + a\alpha_2^{\mathrm{H}} + b\beta_2^{\mathrm{H}} + l\log L^{16} \qquad \text{(a)}$$

$$\mathrm{SP} = c + rR_2 + s\pi_2^* + a\alpha_2^{\mathrm{H}} + b\beta_2^{\mathrm{H}} + l\log L^{16} \qquad \text{(b)}$$

In the present case the dependent variable SP is $\log L - \log L^{\mathrm{Decane}}$ and the explanatory variables are solute parameters as follows: δ_2 is an empirical polarisability correction term, R_2 is a polarisability parameter that reflects the ability of a solute to interact with a solvent through π and n electron pairs, α_2^{H} is the solute hydrogen-bond acidity, β_2^{H} is the solute hydrogen-bond basicity, π_2^* is the solute dipolarity/polarisability, and L^{16} is the Ostwald solubility coefficient of the solute on n-hexadecane at 298 K. The constants *c*, *r*, *s*, *a*, *b*, and *l* in the more useful equation (b) are found by the method of multiple linear regression analysis, and serve to characterise a solvent phase in terms of specific solute/solvent interactions. Application of equation (b) to the five stationary phases examined by Laffort *et al.* shows that the magnitude of these constants is in accord with general chemical principles, and that the present procedure constitutes a new, general method for the characterisation of gas chromatographic stationary phases.

The most widely used method for the classification of stationary phases in gas-liquid chromatography (GLC), is that due to Rohrschneider,[1] either as such, or as subsequently modified by McReynolds.[2] Retention data of solutes are first expressed as Kovats retention indices[3] calculated according to equation (1):

$$I^i = 100\left(\frac{\log \tau^i - \log \tau^m}{\log \tau^{m+1} - \log \tau^m}\right) + 100m \qquad (1)$$

Here, I^i is the retention index of solute *i* on a given stationary phase at a given temperature, τ^i is the adjusted retention time of solute *i*, and τ^{m+1} and τ^m are the adjusted retention times of n-alkanes of carbon number $m + 1$ and m, respectivey. Rohrschneider[1] determined values of I^i for the selected solutes benzene, ethanol, butanone, nitromethane, and pyridine, on squalane (SQ), and on a stationary phase to be investigated (P), and defined a differential set of I^i values through equation (2),

$$\Delta I^i = I_{\mathrm{P}}{}^i - I_{\mathrm{SQ}}{}^i \qquad (2)$$

Then five 'Rohrschneider constants,' *x*, *y*, *z*, *u*, and *s*, one for each of the selected solutes, can be used to characterise the stationary phase, P, according to equation (3), illustrated for the selected solute benzene.

$$x = \Delta I^{\mathrm{benzene}}/100 \qquad (3)$$

An 'overall' stationary phase polarity can also be obtained as the sum of the ΔI^i values for the five test solutes.

McReynolds[2] suggested the use of ten test solutes, rather than five, these being benzene (*x'*), butan-1-ol (*y'*), pentan-2-one (*z'*), nitropropane (*u'*), pyridine (*s'*), 2-methylpentan-2-ol (*h'*), 1-iodobutane (*j'*), oct-2-yne (*k'*), dioxane (*l'*), and *cis*-hydrindane (*m'*). Later workers tended to reduce the number of McReynolds test solutes, for example to the first five solutes.[4] An overall stationary phase polarity can again be calculated as the sum of ΔI^i values ($i = x', y', z', u'$, and s'); for an account of work in this area, the comprehensive review of Budahegyi *et al.*[5] is available.

However, although the Rohrschneider–McReynolds method is the basis of most approaches to the classification of stationary phases, quite recently Poole *et al.*[6] have severely criticised the method on a number of technical and theoretical grounds. Their main technical objection is that alkanes (necessary for the determination of *I* values) are sorbed onto polar stationary phases mainly by interfacial adsorption, rather than by true gas-liquid partitioning. If the I_{P} values are incorrect, then the whole procedure is invalid (for polar phases). A theoretical objection is that the 'overall' polarity, defined as above cannot be a true measure of polarity, since it depends principally on the solubility of the n-alkanes in the stationary phase.[6]

There are other difficulties over the Rohrschneider–McReynolds method. Firstly, the method is entirely restricted to GLC retention data, so that there is no possibility of

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† Part 12: M. H. Abraham, G. S. Whiting, Y. Alarie, J. J. Morris, P. J. Taylor, R. M. Doherty, R. W. Taft, and G. O. Nielsen, *QSAR*, 1990, **9**, 6.

Table 1. Some values of the gas ⟶ solvent methylene increment, $\Delta G_s^\circ(CH_2)$, in kcal mol^{-1} at 298 K.[a]

Solvent	$\Delta G_s^\circ(CH_2)$	Solvent	$\Delta G_s^\circ(CH_2)$
Cyclohexane	−0.76	Propanone	−0.62
Hexadecane	−0.74	Ethanol	−0.61
Decane	−0.74	Dimethylformamide	−0.60
Hexane	−0.74	*N*-Methylpyrrolidi-2-none	−0.56
Benzene	−0.74	Methanol	−0.56
Chlorobenzene	−0.73	Propylene carbonate	−0.48
Tetrachloromethane	−0.71	Dimethyl sulphoxide	−0.48
Octan-1-ol	−0.68	Ethane-1,2-diol	−0.35
Butan-1-ol	−0.66	Water	+0.18
Nitrobenzene	−0.64		

[a] All values from data in ref. 11.

Table 2. Correlations of $\Delta G_s^\circ(CH_2)$ against some solvent parameters.[a]

Intercept	Slope	*n*	*R*	SD
(*a*) All solvents in Table 1				
−0.862	$0.188\,\delta_H^2/100$	19	0.981	0.04
−0.804	$0.370\,\pi_1^*$	19	0.673	0.17
−0.671	$0.043\,\mu_1$	19	0.328	0.21
−0.955	$0.949 f(\varepsilon)$	19	0.554	0.19
−1.396	$0.019\,E_T$	16[b]	0.786	0.15
0.058	$-2.529 f(\eta)$	19	0.376	0.21
−0.399	−0.089 MR	19	0.530	0.19
(*b*) Nonhydroxylic solvents in Table 1				
−0.890	$0.230\,\delta_H^2/100$	13	0.941	0.04
−0.758	$0.189\,\pi_1^*$	13	0.772	0.07
−0.746	$0.046\,\mu_1$	13	0.911	0.04
−0.877	$0.636 f(\varepsilon)$	13	0.859	0.05
−1.273	$0.016\,E_T$	11[c]	0.911	0.04
−0.679	$0.082 f(\eta)$	13	0.024	0.11
−0.570	−0.035 MR	13	0.437	0.10

[a] These are δ_H^2 the Hildebrand cohesive energy density, π_1^* the Kamlet–Taft solvent dipolarity, μ_1 the dipole moment, $f(\varepsilon)$ the dielectric constant function $(\varepsilon - 1)/(2\varepsilon + 1)$, E_T the Reichardt solvent parameter, $f(\eta)$ the refractive index function $(\eta^2 - 1)/(\eta^2 + 2)$, and MR a molar refraction we define as $10f(\eta)V_x$ where V_x is the intrinsic volume. [b] Excluding values for hexadecane, decane, and octan-1-ol. [c] Excluding values for hexadecane and decane.

comparing GLC stationary phases with common solvents. Secondly, the method is far too coarse to allow any analysis of solute-solvent interactions, which are actually the basis of gas-liquid partition, and hence of retention data.

Poole *et al.*,[6] following several other workers,[7–10] suggested that the methylene increment to the gas ⟶ stationary phase transfer, as $\Delta G_s^\circ(CH_2)$ could be taken as a better measure of the overall polarity. Since $\Delta G_s^\circ(CH_2)$ can be obtained from a variety of homologous series, the difficulty over retention processes of alkanes is avoided. However, it is by no means obvious what a general polarity based on $\Delta G_s^\circ(CH_2)$ means. Abraham[11] has published data from which values of $\Delta G_s^\circ(CH_2)$ can be obtained for the n-alkanes in a number of common solvents (see Table 1). Note that since the original measurements were non-chromatographic, the n-alkane difficulty does not arise. We can match the $\Delta G_s^\circ(CH_2)$ values against various solvent polarity parameters, and give simple regression constants in Table 2. For the nonhydroxylic solvents, there are reasonable correlations of $\Delta G_s^\circ(CH_2)$ with solvent dipole movement (μ), or with dielectric constant function $(\varepsilon - 1)/(2\varepsilon + 1)$, or with Reichardt's E_T parameter. But none of these are as good as the solvent cohesive energy density, as $\delta_H^2/100$, and for the total solvent list in Table 2(*a*), only the latter yields a reasonable correlation.* We have examined various double correlations amongst parameters that are not self-correlated, but the only one that is significantly better than the single correlation in $\delta_H^2/100$ is that in equation (4), for nonhydroxylic solvents, where the correlation coefficient, *R*, between δ_H^2 and $f(\eta)$ is only 0.265. Equation (4) can be

$$\Delta G_s^\circ(CH_2) = -0.679 + 0.246\,\delta_H^2/100 - 0.847 f(\eta) \quad (4)$$
$$n = 13 \qquad R = 0.970 \qquad SD = 0.03$$

rationalised using a cavity theory of solution. In order to create a cavity in a solvent, solvent–solvent bonds must be broken in an endoergic process, modelled by δ_H^2. Then on insertion of the solute CH_2 group into the cavity, exoergic CH_2-solvent general dispersion interactions will be set up, modelled at least roughly by $f(\eta)$. The $\Delta G_s^\circ(CH_2)$ increment is therefore not a general polarity parameter in the sense of, say π_1^* or E_T, but reflects a combination of solvent–solvent bond breaking and CH_2-solvent dispersion interactions.

Other workers have moved away from the Rohrschneider–McReynolds method and have attempted to account for retention data on the basis of specific solute–solvent interactions. Ecknig *et al.*[12] characterised solute–solvent interactions in terms of two energy parameters, a nonpolar or dispersion parameter and a polar parameter that includes hydrogen-bonding as an electrostatic effect. The calculation of these parameters, however, is not trivial, and application seems to be restricted to aliphatic solutes only.[13] The UNIFAC solution-of-groups method has been investigated also, but yielded only rough estimates of retention data.[14] A few workers have attempted to characterise stationary phases using indices that include stationary phase acidity and basicity as such. Burns and Hawkes,[15] for example, used retention data on the butan-1-ol–ethyl acrylate pair of solutes to obtain stationary phase basicities, and on pyridine–benzene to obtain stationary phase acidities, but conceded that the obtained indices were rather 'shaky.' Hawkes *et al.*[16] later carried out various spectroscopic studies of solutes in stationary phases and tabulated indices of dispersion forces, polarity, acidity, and basicity for a number of stationary phases (but note that acidity was obtained from retention data on the n-butylamine–n-butyl chloride pair of solutes).

It seems, therefore, to be acknowledged that factors such as dispersion, polarity, acidity, and basicity are important in solute–stationary phase interactions.[13,15,16] In order to quantify these effects, some general system in which both solute and stationary phase are characterised is necessary. The pur-

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* The units of δ_H^2 are cal cm^{-3}, where 1 cal = 4.184 J, and the units of μ are Debyes, where 1 D ≡ 3.336 × 10^{-30} C m.

pose of this paper is to give one set of examples of such a system that can be used for GLC stationary phases, common solvents, and, indeed, any condensed phase.

We start with two equations suggested by Abraham, Doherty, Kamlet, and Taft, and their co-workers,[17–20]

$$SP = c + d\delta_2 + s\pi_2{}^* + a\alpha_2 + b\beta_2 + mV_2 \quad (5)$$

$$SP = c + d\delta_2 + s\pi_2{}^* + a\alpha_2 + b\beta_2 + l\log L^{16} \quad (6)$$

In equations (5) and (6),* SP denotes some property of a series of solutes, for example log V_G or log τ for solutes on a given stationary phase under the same set of conditions. The explanatory variables are δ_2, a polarisability correction term taken as zero except for polyhalogenated aliphatic compounds (0.5) and for aromatic compounds (1.0), $\pi_2{}^*$ the solute dipolarity, α_2 the solute hydrogen-bond acidity, β_2 the solute hydrogen-bond basicity, V_2 the solute volume, and $\log L^{16}$ where L^{16} is the solute Ostwald solubility coefficient on n-hexadecane at 298 K.[21] The constants *c*, *d*, *s*, *a*, *b*, *m*, and *l* are found by multiple linear regression analysis of SP against as many explanatory variables as are statistically significant.

The terms in equations (5) and (6) can be, for the most part, directly identified with particular solute–solvent interactions.[17,18] The $s\pi_2{}^*$ term arises through solute–solvent dipole–dipole or dipole-induced dipole interactions, and hence the magnitude of the *s*-constant will reflect the solvent (or stationary phase) dipolarity. The $a\alpha_2$ term reflects interactions between hydrogen-bond solute acids and a hydrogen-bond solvent base, so that the *a*-constant will now be a measure of the solvent hydrogen-bond basicity. Conversely, the *b*-constant in the $b\beta_2$ term will be a measure of hydrogen-bond solvent acidity. The V_2 and $\log L^{16}$ terms both involve composite interactions, and will include both an endoergic cavity term and an exoergic solute–solvent general dispersion interaction.

There are a number of GLC retention parameters that could be used as the dependent variable (SP) in equations (5) and (6). The standard Gibbs energy of solution of a gaseous solute is given by equation (7), where *L* is the Ostwald solubility

$$-\Delta G_s{}^\circ = RT\ln L = RT\ln(V_G\rho_1) = RT\ln V_G + RT\ln\rho_1 \quad (7)$$

coefficient of the solute in the given solvent, often referred to as *K* the gas-liquid partition coefficient; V_G is the retention volume of the solute at the column temperature,† and ρ_1 is the solvent or stationary phase density. The standard states for $\Delta G_s{}^\circ$ are unit concentration in the gas phase and unit concentration in solution. The most useful dependent variable is log *L*; not only can this be obtained from log V_G values by GLC, but log *L* values can be derived for solution of gaseous solutes in simple solvents If values of ρ_1 are unavailable so that log V_G itself must be used, there is little problem—all the constants in equations (5) and (6) remain the same except for *c* which will alter by log ρ_1. Unfortunately, much retention data in GLC is expressed only as the retention index *I*, equation (1), which on its own is not connected directly to any physicochemical parameter such as log *L* (or log *K*). Only if the so-called *b*-coefficient, herein designated as *B*, is specified for the variation of log V_G with carbon number for n-alkanes can the retention index be reconverted into a suitable parameter for use in equations (5) and (6). Even adjusted retention times, such as log τ values, can be used in these equations since log *L* = log τ + constant.

Results and Discussion

One of the most extensive and carefully determined sets of data is that of Laffort *et al.*[22] who listed retention indices of 240 compounds on five stationary phases at 393 K. Since Laffort *et al.*[22] gave the necessary *B*-values,[23] we can convert the reported values of *I* into log *L* values *via* equation (8),

$$\log L - \log L^{\mathrm{Decane}} = \log L' = \left(\frac{I - 1000}{100}\right)B \quad (8)$$

The constant *c* in equations (5) and (6) is now of little significance, but all the other constants are unaffected by the use of log *L′* rather than log *L* itself. The five Laffort phases are Carbowax, diethyleneglycol succinate (DEGS), polyphenyl ether (PPE), tricyanoethoxypropane (TCEP), and an ester of 'pyromellitic acid and trihydrofluoro alcohol,' known as Zonyl E-7 (ZE7).

Of the explanatory variables, δ_2 is trivial, $\pi_2{}^*$ the Kamlet–Taft dipolarity parameter was as before,[17–20] whilst for α_2 and β_2 we used our new $\alpha_2{}^H$ and $\beta_2{}^H$ hydrogen-bond solute parameters.[24–27] For a few difunctional bases such as anisole we used recently determined 'effective' or 'summation' $\Sigma\beta_2{}^H$ values.[28] The solute volume was taken as McGowan's intrinsic volume,[29] V_x, which has the merit that it can be calculated for any compound of known structure, and values of L^{16} were as before, supplemented by a number of additional values.[28] The general equations (5) and (6) thus take the specific formulation,

$$\log L' = c + d\delta_2 + s\pi_2{}^* + a\alpha_2{}^H + b\beta_2{}^H + mV_x \quad (9)$$

$$\log L' = c + d\delta_2 + s\pi_2{}^* + a\alpha_2{}^H + b\beta_2{}^H + l\log L^{16} \quad (10)$$

We had available a complete set of explanatory variables for 168 solutes out of the 240. Details of the solutes and parameters are in Table 3, and the regressions based on equations (9) and (10) are summarised in Tables 4 and 5. The overall correlation coefficients, *R*, and standard deviations, SD, are not particularly good, but we stress that these refer to 'all solute' regressions. We wish to point out that the purpose of constructing these regressions is to characterise the statinary phases, and not to provide equations that can be used to predict further retention values. The obtained regression equations summarised in Tables 4 and 5 are adequate for the former, but not for the latter, purpose. We note also that as we have found before,[20] equation (10) yields much better regressions than does equation (9) for gas/liquid partition coefficients.‡

We can now examine the constants in equations (9) and (10) to check whether they are chemically reasonable. All five phases are to some extent dipolar, so that the *s*-constant in $s\pi_2{}^*$ should be positive, as observed. The order of stationary phase dipolarity, as measured by the *s*-constant, is TCEP > DEGS > Carbowax > ZE7 ≥ PPE on equation (10), and almost the same on equation (9); this seems chemically quite reasonable. Again, all five phases are hydrogen-bond bases, so that the *a*-constant in $a\alpha_2{}^H$ should be positive. The order of stationary phase basicity is Carbowax > DEGS ≥ TCEP > ZE7 ≥ PPE on both equation (9) and equation (10). As might be expected, the fluoroester ZE7 is both less dipolar and less basic than the ester DEGS. Nominally, the five phases are all non-hydrogen-bond acids, so that the *b*-constant in $b\beta_2{}^H$ should be near zero.

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* We denote solute properties by subscript 2 and solvent properties by subscript 1.

† It is of no value to use $V_G{}^\circ$, the specific retention volume corrected to 273 K, because $V_G{}^\circ$ must be converted back to V_G for use in equation (7).

‡ Except for gas/water partitions, but in this case neither V_x nor $\log L^{16}$ are very significant.[20]

There is a difficulty here, in that over the 168 solute set, the explanatory variable β_2^H is not independent, there being a cross correlation coefficient of 0.673 between β_2^H and π_2^*. The total correlation matrix in terms of R is as follows:

	δ_2	π_2^*	α_2^H	β_2^H
π_2^*	0.302			
α_2^H	−0.188	0.059		
β_2^H	−0.164	0.673	0.373	
$\log L^{16}$	0.052	0.073	−0.032	0.075

We therefore repeated the regressions, excluding the β_2^H parameter, and we conclude that none of the stationary phases has any significant hydrogen-bond acidity [see Tables 5(*a*) and 5(*b*)]

The *l*-constants in $l\log L^{16}$ are all much lower than unity. Part of this will certainly be due to the operating temperature of 393 K instead of 298 K, but part is probably also due to the lessening of general solute–solvent dispersion interactions by comparison to n-hexadecane solvent (at 298 K).

We can conclude that equation (9) and particularly equation (10) are suitable for the characterisation of GLC stationary phases through a set of constants *c*, *d*, *s*, *a*, *b*, and *l*. Unlike Rohrschneider–McReynolds constants, however, those derived from equation (10) yield quantitative information on the propensity of the phase to take part in given solute-stationary phase interactions. The difficulty over n-alkanes on polar phases does not apply to the application of equation (10), because incorporation of alkanes into the solute data set is not essential. Furthermore, an additional advantage of the present method is that it is now possible to compare GLC stationary phases with other condensed phases, for example common solvents. From preliminary regressions[20] we know that the *s*-constant for ethyl acetate is *ca.* 1.8, so that the dipolarity of tricyanoethoxypropane at 393 K is no more than that of a simple ester at 298 K. We hope to apply equation (10) to a variety of solvents, as well as to other GLC stationary phases, in order to obtain a general classification of condensed phases.

There are disadvantages in the use of equations (9) and (10). In order to obtain suitability firm regressions with five explanatory variables, it is necessary to obtain retention data for not less than about 30 solutes. However, since only $\log\tau$ values are needed in order to determine all the constants except *c*, this is not an onerous task. A more important disadvantage is revealed by an examination of the origin of the explanatory variables in equations (9) and (10). The dependent variable is ideally $\log L$ (or $\log K$), *i.e.*, a Gibbs energy related quantity *via* an equilibrium constant. If $\log V_G$, $\log L'$ or $\log\tau$ are used, these quantities are still equivalent to the use of $\log L$ as far as all the terms except the *c*-constant are concerned. Hence for thermodynamic consistency, all the explanatory variables should be Gibbs energy related. There is no difficulty over α_2^H, β_2^H, and $\log L^{16}$ since these are all derived from equilibrium constants, as $\log K$ values.[21,24–27] The variable V_X is not a Gibbs energy term, but since we prefer equation (10) to equation (9) this does not concern us overmuch. A more pressing problem is the δ_2/π_2^* formulism: the δ_2 parameter is simply an empirical correction factor, whilst the π_2^* parameter originates as a spectroscopically determined solvent π_1^* parameter, and is certainly not a Gibbs energy related quantity. Furthermore, π_1^* can only be determined for compounds that are liquids at room temperature, and can be equated to π_2^* only for nonassociated liquids. All other π_2^* values have either been estimated or have been obtained *via* various π_2^*/dipole moment correlations.[19] Because of the indeterminate nature of π_2^*, it becomes impossible to connect the $s\pi_2^*$ term in a regression equation with any specific solute–solvent interaction. In the above discussion we have used the *s*-constant as a measure of 'dipolarity', but more correctly it will represent some blend of polarisability and dipolarity. We set out now our attempts to resolve these difficulties by replacement of the δ_2/π_2^* parameters in equation (10).

Construction of a New General Equation.—We first examine the terms in equation (10), in order to specify more exactly the parameters required to take the place of δ_2 and π_2^*. The α_2^H and β_2^H parameters take care of hydrogen-bond interactions, as spelt out above, and will be retained in any new equation. As we have seen in the introduction, the $\log L^{16}$ parameter is very useful in that it accounts for cavity effects, together with general dispersion interactions of the solute-nonpolar solvent (hexadecane) type. We are then left with solute–solvent dipole–dipole and dipole-induced dipole effects, together with additional dispersion interactions that may loosely be described as polarisability effects. The obvious solute parameter needed to describe dipole–dipole type interactions is the dipole moment (μ_2). Following Kirkwood,[30] we use μ_2^2, which has the advantage that it is very nearly a free energy related quantity.† Various physical quantities can be used to model dispersion/polarisability interactions. We have briefly investigated both the solute molar refraction, MR, and the solute polarisability, but found neither satisfactory when used in combination with μ_2^2, α_2^H, β_2^H, and $\log L^{16}$. The refractive index function, $f(\eta)$, has been used by Fuchs *et al.*[31] with some success, and we give in Table 6 details of regressions using equation (11), with $f(\eta)$ defined by equation (12).

$$\log L' = c + ff(\eta) + q\mu_2^2 + a\alpha_2^H + b\beta_2^H + l\log L^{16} \quad (11)$$

$$f(\eta) = (\eta^2 - 1)/(\eta^2 + 2) \quad (12)$$

The regression equations based on equation (11) are appreciably poorer than those using equation (10). Not only are R and SD poorer, but significant *b*-constants are produced, surely as artifacts. Part of this difficulty may be due to cross-correlations between μ_2^2 and β_2^H ($R = 0.556$) and also between $f(\eta)$ and $\log L^{16}$ ($R = 0.534$), that could be overcome by a more suitable selection of solutes. But $f(n)$ must include interactions already dealt with by the $\log L^{16}$ parameter, hence the coefficients of $\log L^{16}$ in equation (11) are always less than those in equation (10). What is required is a parameter that is more specifically related to the polarisability of the solute as regards interactions due to the presence of polarisable electrons. We start with the solute molar refraction, but for convenience defined in terms of

$$MR_X = 10(\eta^2 - 1)V_X/(\eta^2 + 2) = 10f(\eta)\,V_X \quad (13)$$

the characteristic volume. With V_X in units of (cm^3 mol^{-1})/100, equation (13) will yield MR_X in the more convenient units of (cm^3 mol^{-1})/10. Note that η is taken at 293 K with the sodium-D line. Unlike $f(\eta)$ itself, the molar refraction has the interesting property of being the same (within a few per cent) for a given solute in the gas phase and in solution. Hence although $f(\eta)$ is most conveniently measured on bulk liquids, MR (and MR_X) can be taken as a property of an isolated molecule.‡ In order to

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† Kirkwood[30] showed that the Gibbs energy of a dipole in a dielectric continuum was proportional to μ^2/r^3 where r is the radius of a sphere containing the dipole. Now many functional groups contain a dipole within a sphere of a similar radius, so that the Gibbs energy is approximately proportional to μ^2.

‡ We have confirmed that MR is essentially the same in the gas phase and bulk liquid even for associated compounds such as water and alcohols. The one exception we have noted is acetic acid, probably due to the extensive dimerisation that takes place in the gas phase.

Table 3. The 168 compounds and the parameters used in the regressions.

No.	Compound	δ_2	$f(n)$	R_2	π_2^*	μ_2^2	α_2^H	β_2^H	V_X	$\log L^{16}$
3352	Methanol	0.00	0.203	0.278	0.40	2.890	0.37	0.41	0.308	0.922
3353	Ethanol	0.00	0.221	0.246	0.40	2.856	0.33	0.44	0.449	1.485
3354	Propan-1-ol	0.00	0.234	0.236	0.40	2.822	0.33	0.45	0.590	2.097
3355	Propan-2-ol	0.00	0.230	0.212	0.40	2.756	0.32	0.47	0.590	1.821
3473	Prop-2-en-1-ol, allyl-OH	0.00	0.250	0.341	0.45	2.560	0.33	0.41	0.547	1.996
3356	Butan-1-ol	0.00	0.242	0.224	0.40	2.756	0.33	0.45	0.731	2.601
3358	2-Methylpropan-1-ol	0.00	0.240	0.217	0.40	2.670	0.33	0.45	0.731	2.399
3357	Butan-2-ol	0.00	0.241	0.217	0.40	2.723	0.32	0.47	0.731	2.338
3359	t-Butyl alcohol	0.00	0.236	0.180	0.40	2.657	0.32	0.49	0.731	2.018
3360	Pentan-1-ol	0.00	0.248	0.219	0.40	2.756	0.33	0.45	0.872	3.106
3361	2-Methylbutan-1-ol	0.00	0.248	0.219	0.40	2.890	0.33	0.45	0.872	3.011
3362	3-Methylbutan-1-ol	0.00	0.245	0.192	0.40	2.560	0.33	0.45	0.872	3.011
3440	Cyclopentanol	0.00	0.270	0.427	0.40	2.890	0.32	0.48	0.763	3.270
3368	Hexan-1-ol	0.00	0.252	0.210	0.40	2.890	0.33	0.45	1.013	3.610
3490	(*E*)-Hex-2-en-1-ol	0.00	0.263	0.294	0.45	2.560	0.33	0.41	0.970	3.510
3369	Hexan-2-ol	0.00	0.250	0.187	0.40	2.890	0.32	0.47	1.013	3.340
3370	Hexan-3-ol	0.00	0.251	0.200	0.40	2.890	0.32	0.47	1.013	3.440
3372	2-Methylpentan-2-ol	0.00	0.248	0.169	0.40	2.890	0.32	0.49	1.013	3.181
3374	3-Methylpentan-3-ol	0.00	0.252	0.210	0.40	2.890	0.32	0.49	1.013	3.277
3389	Heptan-1-ol	0.00	0.256	0.211	0.40	2.924	0.33	0.45	1.154	4.115
3492	(*E*)-Hept-2-en-l-ol	0.00	0.267	0.281	0.45	2.560	0.33	0.41	1.111	4.010
3405	Octan-1-ol	0.00	0.258	0.199	0.40	2.958	0.33	0.45	1.295	4.619
3494	(*E*)-Oct-2-en-l-ol	0.00	0.273	0.270	0.45	2.560	0.33	0.41	1.252	4.520
3410	2-Methylheptan-2-ol	0.00	0.256	0.169	0.40	2.890	0.32	0.49	1.295	3.990
3416	Nonan-1-ol	0.00	0.260	0.193	0.40	2.958	0.33	0.45	1.435	5.124
3426	Decan-1-ol	0.00	0.262	0.191	0.40	2.592	0.33	0.45	1.576	5.628
3429	Undecan-1-ol	0.00	0.263	0.181	0.40	2.890	0.33	0.45	1.717	6.130
3430	Dodecan-1-ol	0.00	0.265	0.175	0.40	2.890	0.33	0.45	1.858	6.640
1551	Acetaldehyde	0.00	0.205	0.208	0.67	7.236	0.00	0.40	0.406	1.230
1552	Propionaldehyde	0.00	0.223	0.196	0.65	6.350	0.00	0.40	0.547	1.815
1569	Propenal, acrolein	0.00	0.243	0.324	0.65	9.734	0.00	0.40	0.504	2.110
1553	Butyraldehyde	0.00	0.234	0.187	0.65	7.398	0.00	0.40	0.688	2.270
1554	Isobutyraldehyde	0.00	0.228	0.146	0.65	7.290	0.00	0.40	0.688	2.060
1570	(*E*)-But-2-en-1-al	0.00	0.262	0.387	0.75	12.532	0.00	0.40	0.645	2.570
1556	3-Methylbutanal	0.00	0.237	0.144	0.65	6.859	0.00	0.40	0.829	2.620
1558	Hexanal	0.00	0.244	0.146	0.65	7.290	0.00	0.40	0.970	3.370
1560	Heptanal	0.00	0.248	0.140	0.65	7.290	0.00	0.40	1.111	3.860
1561	Octanal	0.00	0.254	0.160	0.65	7.398	0.00	0.40	1.252	4.380
1590	Benzaldehyde	1.00	0.317	0.820	0.92	7.563	0.00	0.42	0.873	3.985
1651	Propan-2-one	0.00	0.220	0.179	0.71	8.294	0.04	0.50	0.547	1.760
1652	Butan-2-one	0.00	0.231	0.166	0.67	7.618	0.00	0.48	0.688	2.287
1653	Pentan-2-one	0.00	0.237	0.143	0.65	7.290	0.00	0.48	0.829	2.755
1706	Cyclopentanone	0.00	0.262	0.373	0.76	10.890	0.00	0.52	0.720	3.120
1659	Hexan-2-one	0.00	0.243	0.136	0.65	7.023	0.00	0.48	0.970	3.262
1660	Hexan-3-one	0.00	0.243	0.136	0.65	7.290	0.00	0.48	0.970	3.310
1708	Cyclohexanone	0.00	0.269	0.403	0.76	9.000	0.00	0.52	0.861	3.615
1664	Heptan-2-one	0.00	0.247	0.123	0.65	6.812	0.00	0.48	1.111	3.760
1712	Cycloheptanone	0.00	0.274	0.436	0.76	9.610	0.00	0.52	1.002	4.110
1675	Octan-2-one	0.00	0.250	0.108	0.65	7.398	0.00	0.48	1.252	4.257
1713	Cyclo-octanone	0.00	0.279	0.474	0.76	8.762	0.00	0.52	1.143	4.610
1750	Acetophenone	1.00	0.312	0.818	0.90	9.000	0.00	0.51	1.014	4.483
1685	Nonan-2-one	0.00	0.254	0.119	0.65	7.301	0.00	0.48	1.392	4.755
1714	Cyclononanone	0.00	0.280	0.490	0.76	8.123	0.00	0.52	1.284	5.110
1690	Decan-2-one	0.00	0.256	0.108	0.65	7.290	0.00	0.48	1.533	5.260
1715	Cyclodecanone	0.00	0.284	0.527	0.76	7.840	0.00	0.52	1.425	5.610
1722	Carvone	0.00	0.294	0.674	0.80	10.049	0.00	0.49	1.339	5.330
1691	Undecan-2-one	0.00	0.258	0.101	0.65	7.290	0.00	0.48	1.674	5.760
1716	Cycloundecanone	0.00	0.288	0.557	0.76	7.840	0.00	0.52	1.566	6.110
1692	Dodecan-2-one	0.00	0.260	0.103	0.65	7.290	0.00	0.48	1.815	6.260
1717	Cyclododecanone	0.00	0.293	0.588	0.76	7.840	0.00	0.52	1.707	6.600
1352	Diethyl ether	0.00	0.217	0.041	0.27	1.323	0.00	0.45	0.731	2.061
1355	Di-n-butyl ether	0.00	0.242	0.000	0.27	1.369	0.00	0.45	1.294	4.001
1414	Furan	1.00	0.254	0.369	0.50	0.436	0.00	0.15	0.536	1.830
1450	Methyl phenyl ether	1.00	0.303	0.708	0.73	1.904	0.00	0.33	0.916	3.926
2101	Nitromethane	0.00	0.233	0.313	0.85	11.972	0.12	0.25	0.424	1.892
2102	Nitroethane	0.00	0.238	0.270	0.80	13.323	0.00	0.25	0.565	2.367
2103	1-Nitropropane	0.00	0.243	0.242	0.79	13.396	0.00	0.25	0.706	2.850
2143	3-Nitrotoluene	1.00	0.317	0.874	0.97	16.000	0.00	0.34	1.032	4.970
2201	Acetonitrile	0.00	0.212	0.237	0.75	15.366	0.09	0.44	0.404	1.560
2203	1-Cyanopropane	0.00	0.234	0.188	0.68	16.557	0.00	0.44	0.586	2.540

Table 3 (*continued*)

No.	Compound	δ_2	$f(n)$	R_2	π_2^*	μ_2^2	α_2^H	β_2^H	V_X	$\log L^{16}$
2205	1-Cyanobutane	0.00	0.241	0.177	0.68	16.974	0.00	0.44	0.827	3.057
2241	Benzonitrile	1.00	0.308	0.742	0.90	17.472	0.00	0.42	0.871	4.004
2701	Pyridine	1.00	0.299	0.794	0.87	4.796	0.00	0.62	0.675	3.003
2952	Acetic acid	0.00	0.227	0.265	0.60	2.890	0.55	0.43	0.465	1.750
2953	Propanoic acid	0.00	0.235	0.233	0.60	2.890	0.54	0.43	0.606	2.290
2954	Butanoic acid	0.00	0.241	0.210	0.60	2.820	0.54	0.42	0.747	2.830
2956	Pentanoic acid	0.00	0.247	0.205	0.60	2.590	0.54	0.41	0.887	3.380
2957	3-Methylbutanoic acid	0.00	0.244	0.178	0.60	2.790	0.54	0.41	0.887	3.300
2959	Hexanoic acid	0.00	0.251	0.174	0.60	2.490	0.54	0.39	1.028	3.920
2964	Heptanoic acid	0.00	0.251	0.149	0.60	2.790	0.54	0.38	1.169	4.460
2969	Octanoic acid	0.00	0.258	0.150	0.60	2.890	0.54	0.36	1.310	5.000
2975	Nonanoic acid	0.00	0.261	0.132	0.60	2.790	0.54	0.34	1.451	5.550
1860	Methyl acetate	0.00	0.220	0.142	0.60	2.958	0.00	0.40	0.606	1.960
1861	Ethyl acetate	0.00	0.227	0.106	0.55	3.168	0.00	0.45	0.747	2.376
1881	Methyl propanoate	0.00	0.230	0.128	0.55	2.890	0.00	0.45	0.747	2.459
1853	Propyl formate	0.00	0.230	0.132	0.61	3.648	0.00	0.38	0.747	2.413
1862	n-Propyl acetate	0.00	0.234	0.092	0.55	3.419	0.00	0.45	0.887	2.878
1864	n-Butyl acetate	0.00	0.239	0.071	0.55	3.240	0.00	0.45	1.028	3.379
1889	Propyl butanoate	0.00	0.249	0.068	0.55	3.063	0.00	0.45	1.169	3.810
1867	Pentyl acetate	0.00	0.244	0.067	0.55	3.063	0.00	0.45	1.169	3.810
1870	Isopentyl acetate	0.00	0.240	0.051	0.55	3.312	0.00	0.45	1.169	3.740
1892	Isobutyl isobutanoate	0.00	0.242	0.000	0.55	3.240	0.00	0.45	1.310	3.880
1896	Isopentyl isopentanoate	0.00	0.248	0.000	0.55	3.240	0.00	0.45	1.592	4.580
553	Trichloromethane	0.50	0.267	0.425	0.58	1.020	0.20	0.02	0.617	2.480
554	Tetrachloromethane	0.50	0.274	0.458	0.28	0.000	0.00	0.00	0.739	2.823
557	1,2-Dichloroethane	0.50	0.266	0.416	0.81	1.638	0.10	0.05	0.635	2.573
586	1,1,2-Trichloroethene	0.50	0.283	0.524	0.53	0.721	0.12	0.03	0.715	2.997
1038	Benzyl chloride	1.00	0.313	0.821	0.71	3.385	0.00	0.31	0.980	4.290
579	1-Chlorohexane	0.00	0.253	0.201	0.39	3.803	0.00	0.15	1.077	3.710
1002	1,2-Dichlorobenzene	1.00	0.319	0.870	0.80	5.153	0.00	0.03	0.961	4.405
605	Bromoethane	0.00	0.255	0.366	0.48	4.121	0.00	0.17	0.565	2.120
624	1-Bromopentane	0.00	0.266	0.356	0.48	4.840	0.00	0.17	0.988	3.611
637	2-Bromo-octane	0.00	0.267	0.322	0.48	4.000	0.00	0.17	1.411	5.110
651	Iodomethane	0.00	0.313	0.675	0.40	2.624	0.00	0.18	0.508	2.106
670	1-Iodobutane	0.00	0.294	0.628	0.50	4.494	0.00	0.18	0.930	3.628
671	2-Iodobutane	0.00	0.294	0.610	0.50	4.000	0.00	0.18	0.930	3.390
3552	Ethanethiol	0.00	0.259	0.392	0.35	2.459	0.00	0.16	0.554	2.172
3553	n-Propylthiol	0.00	0.263	0.385	0.35	2.280	0.00	0.16	0.695	2.685
3554	Isopropylthiol	0.00	0.256	0.336	0.35	2.560	0.00	0.16	0.695	2.406
3569	Prop-2-en-1-thiol	0.00	0.285	0.542	0.40	2.403	0.00	0.20	0.652	2.510
3555	n-Butylthiol	0.00	0.266	0.382	0.35	2.369	0.00	0.16	0.836	3.243
3556	Isobutylthiol	0.00	0.260	0.356	0.35	2.403	0.00	0.16	0.836	2.880
3558	t-Butylthiol	0.00	0.254	0.281	0.35	2.403	0.00	0.16	0.836	2.558
3601	Thiophene	1.00	0.308	0.684	0.60	0.325	0.00	0.16	0.641	2.943
3559	n-Pentylthiol	0.00	0.269	0.369	0.35	2.403	0.00	0.16	0.977	3.720
3560	Isopentylthiol	0.00	0.272	0.343	0.35	2.403	0.00	0.16	0.977	3.360
3602	2-Methylthiophene	1.00	0.304	0.688	0.40	0.449	0.00	0.14	0.782	3.302
3561	n-Hexylthiol	0.00	0.271	0.361	0.35	2.403	0.00	0.16	1.118	4.220
3603	2,5-Dimethylthiophene	1.00	0.301	0.690	0.40	0.260	0.00	0.16	0.923	3.806
3550	n-Heptanethiol	0.00	0.273	0.357	0.35	2.403	0.00	0.16	1.258	4.720
3562	n-Octylthiol	0.00	0.271	0.353	0.35	2.403	0.00	0.16	1.399	5.310
3563	n-Nonylthiol	0.00	0.271	0.347	0.35	2.403	0.00	0.16	1.540	5.890
3564	n-Decylthiol	0.00	0.270	0.342	0.35	2.403	0.00	0.16	1.681	6.480
3579	Dimethyl sulphide	0.00	0.261	0.404	0.36	2.250	0.00	0.29	0.554	2.238
3580	Diethyl sulphide	0.00	0.265	0.373	0.36	2.310	0.00	0.29	0.836	3.104
3581	Di-n-propyl sulphide	0.00	0.268	0.358	0.36	2.430	0.00	0.29	1.117	4.120
3587	Isopentyl sulphide	0.00	0.272	0.300	0.36	2.560	0.00	0.29	1.681	5.540
3610	Diethyl disulphide	0.00	0.298	0.670	0.64	3.960	0.00	0.22	0.999	4.210
3589	Di-n-butyl sulphide	0.00	0.290	0.345	0.36	2.592	0.00	0.29	1.400	4.950
3585	Methyl-n-propyl sulphide	0.00	0.266	0.380	0.36	2.560	0.00	0.29	0.836	3.240
371	Propene	0.00	0.196	0.103	0.08	0.134	0.00	0.07	0.488	0.946
373	But-1-ene	0.00	0.216	0.100	0.08	0.116	0.00	0.07	0.629	1.491
380	Pent-1-ene	0.00	0.277	0.093	0.08	0.116	0.00	0.07	0.770	2.013
392	Hex-1-ene	0.00	0.234	0.078	0.08	0.116	0.00	0.07	0.911	2.547
406	Hept-1-ene	0.00	0.242	0.092	0.08	0.116	0.00	0.07	1.052	3.063
409	Oct-1-ene	0.00	0.247	0.094	0.08	0.116	0.00	0.07	1.192	3.591
412	(*Z*)-Oct-2-ene	0.00	0.250	0.135	0.08	0.090	0.00	0.07	1.192	3.650
413	2-Ethylhex-1-ene	0.00	0.251	0.139	0.08	0.116	0.00	0.07	1.192	3.510
468	Oct-1-yne	0.00	0.251	0.155	0.20	0.656	0.13	0.20	1.150	3.480
469	Oct-2-yne	0.00	0.257	0.226	0.20	0.656	0.00	0.20	1.150	3.850

Table 3 (*continued*)

No.	Compound	δ_2	$f(n)$	R_2	π_2^*	μ_2^2	α_2^H	β_2^H	V_X	$\log L^{16}$
751	Benzene	1.00	0.295	0.610	0.59	0.000	0.00	0.14	0.716	2.803
752	Toluene	1.00	0.292	0.601	0.55	0.130	0.00	0.14	0.857	3.344
766	Ethylbenzene	1.00	0.292	0.613	0.53	0.348	0.00	0.15	0.998	3.765
843	Styrene	1.00	0.317	0.848	0.55	0.063	0.00	0.18	0.955	3.908
795	Phenylethyne	1.00	0.300	0.679	0.55	0.533	0.12	0.21	0.912	3.715
753	2-Xylene	1.00	0.297	0.663	0.51	0.384	0.00	0.17	0.998	3.937
754	3-Xylene	1.00	0.293	0.623	0.51	0.160	0.00	0.17	0.998	3.864
755	4-Xylene	1.00	0.292	0.613	0.51	0.000	0.00	0.17	0.998	3.858
758	Mesitylene	1.00	0.294	0.649	0.47	0.000	0.00	0.20	1.139	4.399
442	α-Pinene	0.00	0.277	0.446	0.10	0.130	0.00	0.10	1.257	4.200
52	Propane	0.00	0.181	0.000	0.00	0.000	0.00	0.00	0.531	1.050
53	n-Butane	0.00	0.205	0.000	0.00	0.000	0.00	0.00	0.672	1.615
54	Isobutane	0.00	0.197	0.000	0.00	0.000	0.00	0.00	0.672	1.409
55	n-Pentane	0.00	0.219	0.000	0.00	0.000	0.00	0.00	0.813	2.162
58	n-Hexane	0.00	0.229	0.000	0.00	0.000	0.00	0.00	0.954	2.688
287	Cyclohexane	0.00	0.257	0.305	0.00	0.000	0.00	0.00	0.845	2.913
63	n-Heptane	0.00	0.236	0.000	0.00	0.000	0.00	0.00	1.095	3.173
73	2-Methylheptane	0.00	0.240	0.000	0.00	0.000	0.00	0.00	1.236	3.480
74	3-Methylheptane	0.00	0.242	0.000	0.00	0.000	0.00	0.00	1.236	3.510
69	2,3-Dimethylpentane	0.00	0.232	0.000	0.00	0.000	0.00	0.00	1.095	2.841
72	n-Octane	0.00	0.241	0.000	0.00	0.000	0.00	0.00	1.236	3.677
91	n-Nonane	0.00	0.245	0.000	0.00	0.000	0.00	0.00	1.377	4.182
112	2,2,5-Trimethylhexane	0.00	0.242	0.000	0.00	0.000	0.00	0.00	1.377	3.530
126	n-Decane	0.00	0.248	0.000	0.00	0.000	0.00	0.00	1.518	4.686
162	n-Undecane	0.00	0.263	0.000	0.00	0.000	0.00	0.00	1.658	5.191
168	n-Dodecane	0.00	0.254	0.000	0.00	0.000	0.00	0.00	1.799	5.696
174	n-Tridecane	0.00	0.256	0.000	0.00	0.000	0.00	0.00	1.940	6.200
180	n-Tetradecane	0.00	0.258	0.000	0.00	0.000	0.00	0.00	2.081	6.705

Table 4. Regression analysis using equation (9), $n = 168$; $\log L' = c + d\delta_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + mV_X$.

Phase		c	d	s	a	b	m	SD[a]	R[b]
Carbowax		−2.33	0.20	2.29	2.37	−0.53	1.57	0.22	0.960
	SD[c]	0.07	0.06	0.12	0.12	0.17	0.05		
	CL[d]	1.00	0.99	1.00	1.00	0.99	1.00		
DEGS		−2.04	0.25	2.41	2.05	−0.20	1.40	0.24	0.955
	SD	0.07	0.07	0.13	0.13	0.18	0.05		
	CL	1.00	1.00	1.00	1.00	0.74	1.00		
PPE		−2.90	0.22	1.93	0.84	−0.38	1.98	0.22	0.959
	SD	0.07	0.06	0.12	0.12	0.17	0.05		
	CL	1.00	1.00	1.00	1.00	0.97	1.00		
TCEP		−1.95	0.20	2.67	2.02	−0.02	1.32	0.23	0.961
	SD	0.07	0.07	0.13	0.13	0.18	0.05		
	CL	1.00	1.00	1.00	1.00	0.08	1.00		
ZE7		−2.43	0.09	1.91	0.81	0.21	1.59	0.16	0.975
	SD	0.05	0.04	0.09	0.08	0.12	0.04		
	CL	1.00	0.96	1.00	1.00	0.91	1.00		

[a] Overall standard deviation. [b] Overall correlation coefficient. [c] Standard deviation in the constant. [d] Confidence level: 1.00 signifies >0.99.

remove the dispersive part already incorporated in $\log L^{16}$, we then subtract out the value of MR_X for an alkane of the same

$$R_2 = MR_X(\text{observed}) - MR_X(\text{alkane of same } V_X) \quad (14)$$

characteristic volume, equation (4). The latter quantity is readily obtained through an excellent linear regression for the n-alkanes,

$$MR_X(\text{alkane}) = -0.525\,53 + 2.831\,95V_X \quad (15)$$
$$n = 13, R = 0.999\,99, SD = 0.0078$$

Hence knowing $f(\eta)$ and V_X for any solute, MR_X and then R_2 can be calculated *via* equations (13)–(15). For convenience we tabulate R_2 in units of 10^{-1} cm^3, and give a number of typical values in Table 7. Note that by definition $R_2 = 0$ for all n-alkanes, and by calculation R_2 is also zero for branched chain alkanes and for the rare gases as well.

We now use the new polarisability parameter, R_2, in conjunction with μ_2^2, to construct equation (16), that we apply to the same set of 168 solutes as before. Details are in Table 8.

$$\log L' = c + rR_2 + q\mu_2^2 + a\alpha_2^H + b\beta_2^H + l\log L^{16} \quad (16)$$

The quality of the regressions in Table 8 is slightly better than those in Table 6, based on equation (11), but significantly poorer than those in Table 5, based on equation (10). For purposes of characterisation, this might not matter too much, but unfortunately the regressions in Table 8(*a*) show larger dependences on β_2^H that are probably artifacts [compare Table 8 (*a*) with Table 8 (*b*)]. Although there is no significant cross-correlation between R_2 and any other explanatory variable in equation (16), there still remains the connection between μ_2^2 and β_2^H, $r = 0.556$, referred to above. It is possible that for a better selection of solutes without the μ_2^2/β_2^H cross-correlation, equation (16) might perform as well as equation (10), and we intend to investigate this further.

Finally, we suggest that our calculated R_2 values (Table 7) can replace the empirical δ_2 values in equation (10) to yield equation (17). Details of regressions using equation (17) are in

$$\log L' = c + rR_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + l\log L^{16} \quad (17)$$

Table 9. In terms of overall standard deviation and correlation coefficient, these regressions are the best we have obtained, being slightly better than those given in Table 5. We have also investigated replacement of δ_2 by R_2 in equation (9), but, as usual, find that equations using V_X are considerably poorer than those using $\log L^{16}$

Table 5. Regression analysis using equation (10), $n = 168$; $\log L' = c + d\delta_2 + s\pi_2{}^* + a\alpha_2{}^H + b\beta_2{}^H + l\log L^{16}$.

Phase		c	d	s	a	b	l	SD	R
(*a*) Carbowax		−2.07	0.05	1.55	2.13	−0.17	0.446	0.14	0.985
	SD	0.04	0.04	0.07	0.07	0.10	0.008		
	CL	1.00	0.83	1.00	1.00	0.89	1.00		
DEGS		−1.81	0.12	1.76	1.84	0.11	0.399	0.16	0.978
	SD	0.04	0.05	0.09	0.09	0.12	0.010		
	CL	1.00	0.99	1.00	1.00	0.64	1.00		
PPE		−2.54	0.04	1.01	0.53	0.08	0.554	0.11	0.990
	SD	0.03	0.03	0.06	0.06	0.08	0.007		
	CL	1.00	0.77	1.00	1.00	0.66	1.00		
TCEP		−1.74	0.07	2.06	1.82	0.28	0.380	0.16	0.981
	SD	0.04	0.05	0.09	0.09	0.12	0.010		
	CL	1.00	0.88	1.00	1.00	0.98	1.00		
ZE7		−2.10	−0.05	1.17	0.56	0.59	0.434	0.13	0.984
	SD	0.03	0.04	0.07	0.07	0.10	0.008		
	CL	1.00	0.84	1.00	1.00	1.00	1.00		
(*b*) Carbowax		−2.06	0.08	1.46	2.08		0.446	0.14	0.985
	SD	0.04	0.03	0.05	0.07		0.008		
	CL	1.00	0.98	1.00	1.00		1.00		
DEGS		−1.81	0.10	1.82	1.87		0.400	0.16	0.978
	SD	0.04	0.04	0.06	0.08		0.010		
	CL	1.00	0.98	1.00	1.00		1.00		
PPE		−2.54	0.02	1.05	0.55		0.555	0.11	0.990
	SD	0.03	0.03	0.04	0.05		0.007		
	CL	1.00	0.61	1.00	1.00		1.00		
TCEP		−1.73	0.02	2.21	1.90		0.382	0.16	0.981
	SD	0.04	0.04	0.06	0.08		0.010		
	CL	1.00	0.40	1.00	1.00		1.00		
ZE7		−2.09	−0.16	1.50	0.72		0.438	0.14	0.980
	SD	0.04	0.03	0.05	0.07		0.009		
	CL	1.00	0.99	1.00	1.00		1.00		

[a] These are the preferred equations.

Table 6. Regression analysis using equation (11), $n = 168$; $\log L' = c + ff(\mathrm{n}) + q\mu_2{}^2 + a\alpha_2{}^H + b\beta_2{}^H + mV_X$.

Phase		c	f	q	a	b	l	SD	R
Carbowax		−3.48	7.61	0.59	2.34	0.55	0.370	0.19	0.971
	SD	0.16	0.67	0.005	0.11	0.12	0.014		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
DEGS		−3.62	9.56	0.67	2.06	0.92	0.304	0.22	0.961
	SD	0.18	0.77	0.006	0.13	0.14	0.016		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
PPE		−3.56	5.37	0.038	0.66	0.56	0.500	0.14	0.985
	SD	0.11	0.48	0.004	0.08	0.09	0.010		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
TCEP		−3.67	10.26	0.080	2.09	1.21	0.278	0.23	0.961
	SD	0.19	0.81	0.006	0.13	0.15	0.017		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
ZE7		−2.55	2.84	0.051	0.72	1.04	0.409	0.17	0.972
	SD	0.14	0.58	0.005	0.10	0.11	0.012		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		

Table 7. Some values of the molar refraction parameter, R_2, and the 'correction factor', δ_2.

Solute	$R_2/10^{-1}$ cm^3	δ_2
Rare gases	0	0
Alkanes	0	0
Cyclohexane	0.305	0
But-1-ene	0.100	0
But-1-yne	0.178	0
Benzene	0.610	1
1-Chlorobutane	0.210	0
1-Bromobutane	0.360	0
1-Iodobutane	0.628	0
Dichloromethane	0.387	0.5
Tetrachloromethane	0.458	0.5
Chlorobenzene	0.718	1
Butan-2-one	0.166	0
Diethyl ether	0.041	0
Ethyl acetate	0.106	0
Dimethylformamide	0.367	0
Butan-1-ol	0.224	0
n-Butylamine	0.224	0
Acetophenone	0.818	1
Methyl phenyl ether	0.708	1
Ethyl benzoate	0.663	1
Phenol	0.805	1
Aniline	0.955	1

Table 8. Regression analysis using equation (16), $n = 168$; $\log L' = c + rR_2 + q\mu_2{}^2 + a\alpha_2{}^H + b\beta_2{}^H + l\log L^{16}$.

Phase		c	r	q	a	b	l	SD	R
(*a*) Carbowax		−1.98	0.86	0.052	2.30	0.53	0.438	0.17	0.976
	SD	0.05	0.06	0.005	0.10	0.10	0.011		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
DEGS		−1.74	1.10	0.059	2.03	0.89	0.389	0.19	0.971
	SD	0.05	0.07	0.005	0.11	0.12	0.012		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
PPE		−2.50	0.62	0.033	0.64	0.55	0.548	0.12	0.988
	SD	0.03	0.04	0.003	0.07	0.08	0.008		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
TCEP		−1.67	1.16	0.071	2.05	1.19	0.369	0.20	0.970
	SD	0.05	0.07	0.006	0.12	0.13	0.013		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
ZE7		−1.99	0.34	0.048	0.71	1.04	0.434	0.16	0.974
	SD	0.04	0.06	0.004	0.09	0.10	0.010		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
(*b*) Carbowax		−1.92	0.85	0.068	2.56		0.444	0.18	0.972
	SD	0.05	0.07	0.004	0.09		0.011		
	CL	1.00	1.00	1.00	1.00		1.00		
DEGS		−1.63	1.08	0.084	2.47		0.398	0.22	0.961
	SD	0.06	0.08	0.005	0.11		0.014		
	CL	1.00	1.00	1.00	1.00		1.00		
PPE		−2.44	0.61	0.049	0.91		0.553	0.14	0.984
	SD	0.03	0.05	0.003	0.07		0.009		
	CL	1.00	1.00	1.00	1.00		1.00		
TCEP		−1.50	1.14	0.105	2.64		0.382	0.25	0.954
	SD	0.06	0.09	0.005	0.12		0.016		
	CL	1.00	1.00	1.00	1.00		1.00		
ZE7		−1.88	0.32	0.078	1.22		0.445	0.21	0.956
	SD	0.05	0.07	0.004	0.10		0.013		
	CL	1.00	1.00	1.00	1.00		1.00		

Table 9. Regression analysis using equation (17), $n = 168$; $\log L' = c + rR_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + l\log L^{16}$

Phase		c	r	s	a	b	l	SD	R
(*a*) Carbowax		−2.07	0.25	1.40	2.13	−0.05	0.442	0.13	0.986
	SD	0.03	0.06	0.08	0.07	0.10	0.008		
	CL	1.00	1.00	1.00	1.00	0.42	1.00		
DEGS		−1.84	0.43	1.53	1.83	0.28	0.393	0.15	0.982
	SD	0.04	0.07	0.09	0.08	0.11	0.009		
	CL	1.00	1.00	1.00	1.00	0.98	1.00		
PPE		−2.56	0.25	0.85	0.53	0.21	0.550	0.10	0.991
	SD	0.03	0.05	0.06	0.05	0.08	0.006		
	CL	1.00	1.00	1.00	1.00	0.99	1.00		
TCEP		−1.76	0.36	1.84	1.81	0.45	0.374	0.15	0.984
	SD	0.04	0.07	0.09	0.08	0.11	0.009		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
ZE7		−2.08	−0.24	1.31	0.56	0.48	0.438	0.12	0.985
SD		0.03	0.06	0.07	0.06	0.09	0.008		
	CL	1.00	1.00	1.00	1.00	1.00	1.00		
(*b*)[a] Carbowax		−2.07	0.26	1.37	2.11		0.442	0.13	0.986
	SD	0.03	0.05	0.05	0.06		0.008		
	CL	1.00	1.00	1.00	1.00		1.00		
DEGS		−1.83	0.35	1.70	1.92		0.396	0.15	0.981
	SD	0.04	0.06	0.06	0.07		0.009		
	CL	1.00	1.00	1.00	1.00		1.00		
PPE		−2.55	0.19	0.98	0.59		0.552	0.11	0.991
	SD	0.03	0.04	0.04	0.05		0.007		
	CL	1.00	1.00	1.00	1.00		1.00		
TCEP		−1.75	0.23	2.12	1.94		0.379	0.16	0.982
	SD	0.04	0.06	0.06	0.08		0.010		
	CL	1.00	1.00	1.00	1.00		1.00		
ZE7		−2.07	0.38	1.61	0.70		0.442	0.13	0.983
	SD	0.03	0.05	0.05	0.06		0.008		
	CL	1.00	1.00	1.00	1.00		1.00		

[a] These are the preferred equations.

In our view, equation (17) represents the most satisfactory regression equation we have been able to construct. Analysis of the constants follows closely our analysis using equation (10). Although the analysis *via* equation (17) is only slightly better than that through equation (10), we prefer the former because the R_2 parameter is a well-defined explanatory variable that refers to a specific type of solute–solvent phase interaction. From the method of determination of R_2, as well as from inspection of R_2 values, it follows that the rR_2 term in equation (17) is a quantitative measure of the ability of a solute to interact with the solvent through solute π (mainly) or n-electron pairs. Furthermore, R_2 is a reasonably independent explanatory variable; cross-correlation coefficients between R_2 and the other explanatory variables in equations (16) and (17) are:

π_2^*	μ_2^2	α_2^H	β_2^H	$\log L^{16}$
0.503	0.175	−0.152	0.025	0.124

There is bound to be some correlation between R_2 and π_2^* because we have still not succeeded in subtracting all the polarisability contribution from π_2^*. However, equation (17) does go some way to so doing.

Table 10. The characterisation of stationary phases at 393 K.

Phase	c^a	d	s	a	l
Carbowax	−2.06	0.08	1.46	2.08	0.445
DEGS	−1.81	0.10	1.82	1.87	0.400
PPE	−2.54	0.02	1.05	0.55	0.555
TCEP	−1.73	0.02	2.21	1.90	0.382
ZE7	−2.54	0.16	1.50	0.72	0.438
	c	r	s	a	l
Carbowax	−2.07	0.26	1.37	2.11	0.442
DEGS	−1.83	0.35	1.70	1.92	0.396
PPE	−2.55	0.19	0.98	0.59	0.552
TCEP	−1.75	0.23	2.12	1.94	0.379
ZE7	−2.07	−0.38	1.61	0.70	0.442
	c	r	q	a	l
Carbowax	−1.92	0.85	0.068	2.56	0.444
DEGS	−1.63	1.08	0.084	2.47	0.398
PPE	−2.44	0.61	0.049	0.91	0.553
TCEP	−1.50	1.14	0.105	2.64	0.382
ZE7	−1.88	0.32	0.078	1.22	0.445

[a] Note that this constant includes the term $\log L^{\text{Decane}}$, see equation (8).

Conclusions

A number of equations can be constructed for the characterisation of gas chromatographic phases, and, indeed, any solvent phase, through a series of constants that refer to specific solute–solvent interactions. Our preferred equation (17) leads to a set of constants *c*, *r*, *s*, *a*, *b*, and *l* of which *r* refers to interactions through solute π- and n- electron pairs, *s* to interactions of the dipole–dipole and dipole-induced dipole type (together with some polarisability effects), *a* to solute hydrogen-bond acid/solvent hydrogen-bond base interactions, *b* to solute hydrogen-bond base/solvent hydrogen-bond acid interactions and *l* to a combination of general dispersion forces plus cavity effects. The methodology does not suffer from the technical deficiences of the Rohrschneider–McReynolds method, as outlined by Poole *et al.*,[6] and can be applied to any condensed phase. We list in Table 10, the characteristic constants for the Laffort phases, using equations that omit the β_2^H explanatory variable. The dipolarity of the three phases, using either π_2^* or μ^2 as a probe, is always in the order:

$$\text{TCEP} > \text{DEGS} > \text{ZE7} > \text{Carbowax} > \text{PPE}$$

and the hydrogen-bond basicity of the phases, as given by the *a*-constant, is best represented by the order,

$$\text{Carbowax} > \text{TCEP} \geq \text{DEGS} > \text{ZE7} > \text{PPE}$$

The ability of the phase to interact with solutes specifically through π- and n- solute electron pairs is given by the *r*-constant in the rR_2 term. There is not very good quantitative agreement between equations (16) and (17), but both equations show that the fluorinated solvent ZE7 has the least ability to take part in π- and n-interactions.

We aim to extend this method of characterisation to other stationary phases and to common solvents, and hope to report further in the near future.

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