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Hydrogen bonding

XV. A new characterisation of the McReynolds 77-stationary phase set

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ABSTRACT

The following equation has been applied to all the phases in the McReynolds 77-stationary phase set.

$$\log V_G^0 = c + rR_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + l \log L^{16}$$

In this equation, V_G^0 is the specific retention volume for a series of solutes on a given stationary phase, and the explanatory variables are R_2 a modified solute molar refraction, π_2^* the solute dipolarity, α_2^H the solute hydrogen-bond acidity, β_2^H the solute hydrogen-bond basicity, and $\log L^{16}$ where L^{16} is the solute Ostwald absorption coefficient on hexadecane at 25°C. The constants in the equation are obtained by multiple linear regression analysis, using about 150 data points in each regression, and values of *r, s, a, b* and *l* are regarded as characteristic constants of the phases that serve to classify the 77-phase set. It is shown that the classification of the phases into clusters is in accord with chemical principles, and is in excellent agreement with previous work using hierarchical clustering, minimum spanning tree techniques, and pattern cognition methods. The above equation allows the factors that lead to gas–liquid chromatographic separations to be identified, and provides quantitative information on the various solute–solvent interactions that give rise to these factors.

INTRODUCTION

The largest sets of gas chromatographic retention data are those of McReynolds, who determined retention volumes (V_G^0) and retention indices (I) of 376 solutes on 77 phases at two temperatures [1], and retention indices of 10 solutes on 226 phases at 120°C [2]. Numerous workers have classified both the 77-phase set and the 226-phase set by various methods. McReynolds himself [2] assigned a single polarity index to the 226 stationary phases, using the sum of the ΔI values for benzene, butanol, 2-pentanone, nitropropane and pyridine. Later workers refined this method [3] and also calculated a polarity index from the Gibbs energy of solvation of the methylene increment, $\Delta G_s^0(CH_2)$, on a given stationary phase [4]. Other workers assigned a number of characteristic parameters to phases. Thus Figgins *et al.* [5] derived ΔG_s^0 values for six functional groups on 75 of the 226-phase set, and Fellous *et al.* [6] assigned a polarity index (ρ^*) to the same six functional groups on 72 of the 226-phase set.

Various sophisticated methods have been used to classify the McReynolds phases into groups. They include nearest neighbour techniques [7], information theory [8], numerical taxonomy [8,9], principal components analysis [10], pattern cognition methods [11,12] and factor analysis [13]. All these methods reduce the 226-phase set or the 77-phase set to a smaller number of clusters each of which represents a collection of similar phases. This is a very useful and helpful outcome, but, in addition, several of these methods lead to the estimation of the number of factors that influence chromatographic retention data. Wold and Andersson [10] suggested three main factors, (1) polarity, (2) a factor difficult to identify and (3) a factor that was due to hydrogen-bonding of the phase with alcohols. Chastrette [13] showed that five factors accounted for 99% of the total variance: three factors were difficult to account for, and the other two were polarity and a factor connected to, but not identical with, hydrogen-bonding. A polarity factor was identified by McCloskey and Hawkes [14], who also suggested that a factor related to the ability of a phase to retain *cis*-hydrindane was important.

It seems, therefore, that although a single "polarity" parameter is still often used to characterise stationary phases [4,15], analytical methods suggest that a number of factors must be involved, perhaps three [10] to five [13], although identification of these factors with particular chemical interactions has not proved possible. Our analysis starts with a model for solvation of a solute, and then deduces from the model various possible interactions. Once these interactions are set out, the necessary parameters required to quantify these interactions have to be obtained (from data other than the chromatographic results to be analysed). These parameters then, in effect, take the place of the various factors identified by methods such as principal components analysis [10] or factor analysis [13].

On our model, the process of dissolution of a gaseous solute into a liquid stationary phase or solvent can conceptually be broken down into a number of stages, *viz.* (1) the creation of a cavity in the phase of suitable size, (2) reorganisation of solvent molecules round the cavity and (3) introduction of the solute into the cavity. The first stage involves the endoergic breaking of solvent–solvent bonds: the larger the solute, the more bonds are broken to create a cavity, and the more endoergic is the process. On this step alone, the larger the solute the less soluble it would be, and the smaller would be the retention volume (V_G^0) or the Ostwald solubility coefficient (L). The second stage is not very important in terms of Gibbs energy, although it probably is in terms of enthalpy and entropy. In the third stage, various solute–solvent interactions will be set up, all of which will be exoergic and will lead to increased solubility of the solute. Possible interactions include: (i) General dispersion interactions that will invariably be larger or more exoergic the larger is the solute. It is these interactions that account for the solubility of inert solutes such as the alkanes. And since such solutes are more soluble the larger they are, these dispersion interactions must be strong enough to overcome the endoergic cavity effect. (ii) Dipolar interactions, including dipole–dipole or dipole–induced dipole effects. (iii) Hydrogen-bonding interactions between solute acid–solvent base and solute base–solvent acid. (iv) Possible specific interactions involving π- or n-electron pairs. In view of this complexity of solute–solvent systems, it is not surprising that only limited identification of the factors governing such systems has hitherto been made, but it is clearly of considerable importance if stationary phases could be characterised in terms of these fundamental interactions.

We have now developed solute parameters that, we believe, correspond to either simple fundamental properties, or to known combinations of properties [16–23]. These are as follows: R_2 a modified polarisability parameter that characterises the ability of a solute to interact via π- or n-electron pairs [16,17], δ_2 a polarisability correction term [18–20] taken as zero except for polyhalogenated aliphatics (0.5) or aromatics (1.0) and which is probably an approximation toR_2, π_2^* the solute dipolarity[a] [18–20], α_2^H the solute hydrogen-bond acidity [21], β_2^H the solute hydrogen-bond basicity [22] and log L^{16} where L^{16} is the solute Ostwald solubility coefficient on hexadecane at 25°C [23]. This latter parameter is a combination of a cavity term and a general dispersion interaction term [24]. Various multiple linear regression equations can then be constructed to account for solubility-related properties (SP) of a series of solutes in a given solvent or stationary phase, eqns. 1–3, where SP can be V_G^0, L (or K, the gas–liquid partition coefficient), but *cannot* be the retention index.

$$\log \mathrm{SP} = c + rR_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + l \log L^{16} \quad (1)$$

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

$$\log \mathrm{SP} = c + rR_2 + q\mu_2^2 + a\alpha_2^H + b\beta_2^H + l \log L^{16} \quad (3)$$

In eqn. 3, μ_2 is the solute dipole moment. We have applied eqns. 1–3 to a number of sets of gas chromatographic retention data, and also to the solubility of gases and vapours in some common solvents, with considerable success [16,17,25]. Now since the parameters, or explanatory variables, in eqns. 1–3 represent solute properties, the various constants found by multiple linear regression analyses, will represent solvent or stationary phase properties. The most useful equation in this respect is eqn. 1 for which we have r the tendency of the phase to interact with π- and n-solute electron pairs, s the phase dipolarity, a the phase hydrogen-bond basicity (because basic phases will interact with acidic solutes), b the phase hydrogen-bond acidity, and l representing a combination of general dispersion interactions and cavity effects. These constants r, s, a, b and l (together with possibly q, another measure of phase dipolarity) thus serve to characterise the phase in terms of particular chemical interactions. That up to five constants are needed to characterise a given stationary phase reflects the complexity of solute–solvent interactions. The number of constants,

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[a] We use this term in the Kamlet–Taft sense [18], namely the ability of a molecule to undergo molecular interactions of a dipole–dipole or a dipole–induced dipole nature. Thus dioxane and 1,4-dichlorobenzene are regarded as "dipolar", even though they have no permanent dipole moment.

however, is certainly in accord with principal components analysis [10] and factor analysis [13], which both show that several factors are required to account for retention data.

RESULTS

We now apply eqns. 1–3 to the data of McReynolds [1] on 367 solutes on 77 phases. Of the solutes studied, we have all the necessary parameters for about 160, and our analysis uses up to 157 solutes on the 77 phases at two temperatures[a]. As pointed out, above, retention indices are not suitable for use as SP values in eqns. 1–3, and all our analyses are in terms of the log V_G^0 values reported by McReynolds [1]. We first test, as a necessary preliminary, whether the solute parameters used as explanatory variables are, indeed, independent. In Table I are given the correlation constants, R, between the explanatory variables in eqn. 1. It can be seen that the intercorrelations are insignificant, with the possible exception of that between π_2^* and β_2^H for which $R = 0.474$ (and $R^2 = 0.225$ only). We also test eqns. 1–3 for two typical phases, ethyleneglycol adipate and dibutyltetrachlorophthalate; results are in Table II. Both the overall correlation coefficient and the standard deviation, S.D., are almost identical for eqn. 1 and eqn. 2. Since the molar refraction parameter R_2 can be identified with a specific type of solute–solvent interaction, whereas the empirical δ_2 parameter cannot, we shall list results in terms of the preferred eqn. 1 only. Although the correlations in terms of eqn. 3 are quite useful, they are in all cases not as good as eqn. 1, and so we shall not give all the details of eqn. 3, but list where necessary values of the q constant only.

TABLE I

CORRELATION COEFFICIENTS BETWEEN THE EXPLANATORY VARIABLES, FOR THE 155-SOLUTE DATA SET USED FOR FLEXOL

	R_2	π_2^*	α_2^H	β_2^H
π_2^*	0.295			
α_2^H	0.111	−0.210		
β_2^H	−0.243	0.474	0.247	
log L^{16}	0.016	−0.171	−0.061	−0.169

The results of application of eqn. 1 to the entire set of stationary phases at 120°C are summarised in Table III, where also the q constant in eqn. 3 is given. For a few phases, data were available at 80 and 100°C only, and we have estimated the various constants at 120°C from values at the lower temperatures. For completeness, we applied the various equations to results at the other given temperatures used in the work of McReynolds [1], and details are shown in Table IV. Before attempting to

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[a] McReynolds studied a large number of difunctional compounds for which we lack most of the required parameters in eqns. 1 and 2; these include many formals, acetals, dihydric alcohols, etc. Note that not all solutes were studied on all phases, so that the number of solutes used in our regressions varies from 130 to 157.

TABLE II

COMPARISON OF EQNS. 1–3 IN REGRESSIONS OF LOG V_G^0 AT 120°C

S.D. = Overall standard deviation; *R* = overall correlation coefficient; *n* = number of solutes.

Eqn.	*c*	*r*	*d*	*s*	*q*	*a*	*l*	S.D.	*R*	*n*
Ethyleneglycol adipate										
1	−0.900	0.357		1.425		1.720	0.443	0.093	0.9857	143
	0.038[a]	0.048		0.048		0.053	0.007			
2	−0.871		0.116	1.480		1.867	0.438	0.094	0.9849	143
	0.038		0.030	0.047		0.053	0.007			
3	−0.360	0.784			0.073	1.405	0.394	0.160	0.9476	143
	0.055	0.079			0.006	0.089	0.013			
Dibutyltetrachlorophthalate										
1	−0.615	0.249		0.692		0.600	0.600	0.048	0.9969	150
	0.019	0.025		0.025		0.028	0.004			
2	−0.615		0.112	0.752		0.687	0.599	0.050	0.9967	150
	0.020		0.016	0.025		0.029	0.004			
3	−0.410	0.547			0.038	0.420	0.586	0.070	0.9920	150
	0.024	0.039			0.003	0.040	0.006			

[a] These are the standard deviations in the constants.

classify the phases, we note that the correlation eqn. 1 yields results that are reasonably good for "all solute" correlations, and, as we shall see, these results are chemically sensible. Thus the *s*, *a* and *b* constants, when statistically significant, are always positive, because increase in solute–solvent interactions must lead to an increase in solubility of the gaseous solute, and hence to an increase in V_G^0. The *r* constant is nearly always positive, except in the case of fluorinated phases, *e.g.* Dow fluid 1265, where the polarisability is even less than in hydrocarbon systems. As mentioned in the introduction, the *l* constant reflects a combination of an endoergic cavity term and an exoergic solute–solvent general dispersion interaction term. The latter always dominates, giving rise to positive *l* constants.

The effect of temperature is very important with regard to characterisation of solubility-related phenomena, although it has generally been overlooked as regards characterisation of stationary phases. In general, the main characteristic constants *s*, *a*, *b* and *l*, all decrease, often quite markedly, with temperature. Now if the relevant solute–solvent interactions are not only exoergic but are exothermic as well, the Van 't Hoff equation requires that these interactions will decrease with increase in temperature, hence leading to a decrease in the numerical values of the characteristic constants. On thermodynamic grounds it thus follows that any correlation equation set up in terms of solute–solvent or solute–stationary phase interactions must incorporate this temperature dependence. Our eqn. 1 does so via the characteristic constants.

As a final check on our method of analysis, we can compare regression equations obtained from the set of solutes used by McReynolds [1] with those [16] from the quite different set of solutes used by Patte *et al.* [26] for Carbowax 1540, diethyleneglycolsuccinate, polyphenyl ether and Zonyl-E7. Details are in Table V, and show that there is very good agreement between the two sets of regressions using eqn. 1.

TABLE III

CLASSIFICATION OF PHASES AT 120 °C

S.D. and R are the overall deviation and correlation coefficient on application of eqn. 1 to log V_G^0. The number of data points is No. q = The coefficient of μ_2^2 in eqn. 3.

Group	Stationary phase	Characteristic constants in eqn. 1					S.D.	R	No	q
		c	r	s	a	l				
1	Squalane[a]	−0.33	0.12	0.02	0.00	0.619	0.026	0.9990		0.001
2	Apiezon M	−0.45	0.26	0.10	0.11	0.600	0.035	0.9982	147	0.006
	Apiezon N	−0.48	0.27	0.12	0.10	0.601	0.037	0.9978	149	0.008
	Apiezon J	−0.48	0.27	0.13	0.13	0.594	0.034	0.9984	148	0.010
	Apiezon L	−0.48	0.27	0.14	0.13	0.596	0.036	0.9982	149	0.006
3	Versilube P50	−0.37	0.03	0.25	0.17	0.538	0.036	0.9978	149	0.010
	SE-31	−0.36	0.03	0.24	0.17	0.520	0.039	0.9971	156	0.012
	SE-30	−0.32	0.03	0.27	0.29	0.523	0.040	0.9971	152	0.014
	SE-30 NPGA	−0.40	0.06	0.27	0.33	0.525	0.042	0.9969	152	0.016
	SE-52	−0.38	0.06	0.32	0.22	0.532	0.041	0.9971	155	0.018
4	Dioctylsebacate	−0.35	0.12	0.49	0.79	0.594	0.047	0.9967	153	0.029
	Di-2-ethylhexylsebacate	−0.36	0.13	0.51	0.83	0.591	0.045	0.9969	153	0.028
	Tripelargonate	−0.42	0.16	0.53	0.82	0.583	0.051	0.9964	151	0.032
	Isooctyldecyladipate	−0.37	0.13	0.55	0.81	0.586	0.048	0.9964	154	0.031
	Di-2-ethylhexyladipate	−0.36	0.13	0.55	0.87	0.590	0.047	0.9967	150	0.030
	Diisodecylphthalate	−0.52	0.13	0.65	0.73	0.589	0.055	0.9958	155	0.038
	Dioctylphthalate	−0.52	0.14	0.67	0.77	0.587	0.053	0.9960	153	0.039
5	Ucon LB-1715	−0.56	0.18	0.71	1.22	0.543	0.072	0.9923	153	0.038
	Flexol 8N8	−0.48	0.11	0.73	1.27	0.573	0.065	0.9932	155	0.043
	Pluronic L81	−0.49	0.20	0.77	1.29	0.537	0.075	0.9913	152	0.040
6	Polyphenyl ether, 5 rings	−0.70	0.21	0.88	0.54	0.564	0.064	0.9940	155	0.048
	Polyphenyl ether, 6 rings	−0.74	0.21	0.90	0.56	0.563	0.066	0.9935	155	0.048
7	Tricresylphosphate	−0.68	0.15	1.06	1.23	0.550	0.074	0.9930	154	0.057
	Sucrose acetate isobutanoate	−0.56	0.05	1.05	1.29	0.509	0.071	0.9928	157	0.056
8	Hallcomid M18	−0.35	0.11	0.60	1.55	0.592	0.062	0.9947	154	0.037
	Hallcomid M180L	−0.45	0.10	0.71	1.59	0.592	0.068	0.9930	153	0.040

9	Pluronic L42	−0.52	0.21	0.88	1.45	0.529	0.081	0.9898	154	0.045
	Pluronic L72	−0.54	0.17	0.89	1.41	0.531	0.077	0.9917	153	0.042
	Pluronic L61	−0.53	0.20	0.91	1.42	0.526	0.079	0.9905	151	0.044
	Pluronic L63	−0.54	0.24	0.92	1.46	0.519	0.080	0.9900	153	0.046
	Polytergent J300	−0.55	0.16	0.94	1.49	0.536	0.081	0.9901	154	0.052
	Pluronic P84	−0.57	0.20	0.94	1.44	0.516	0.079	0.9908	152	0.047
	Pluronic P85	−0.57	0.28	0.94	1.46	0.512	0.082	0.9902	153	0.052
	Pluronic L44	−0.56	0.26	0.96	1.52	0.515	0.084	0.9899	154	0.049
	Oronite NIW	−0.62	0.25	0.96	1.46	0.524	0.085	0.9898	155	0.053
	Ucon HB-2000	−0.60	0.28	0.97	1.48	0.514	0.081	0.9907	154	0.053
	Ethofat 60-25	−0.60	0.26	0.99	1.54	0.523	0.078	0.9916	154	0.052
	Pluronic P65	−0.60	0.28	1.01	1.50	0.513	0.086	0.9893	155	0.050
	Pluromic P46	−0.61	0.30	1.02	1.56	0.505	0.085	0.9893	154	0.052
	Tergitol NPX	−0.57	0.19	1.02	1.47	0.518	0.078	0.9917	154	0.058
10	Neopentylglycoladipate, term	−0.68	0.21	1.08	1.45	0.510	0.070	0.9929	152	0.057
	Ethyleneglycolsebacate	−0.78	0.27	1.10	1.44	0.518	0.078	0.9911	145	0.054
	Diethyleneglycolsebacate	−0.76	0.32	1.14	1.45	0.498	0.074	0.9910	141	0.052
	Neopentylglycoladipate	−0.67	0.24	1.14	1.47	0.491	0.073	0.9916	150	0.060
	Neopentylglycolsuccinate	−0.71	0.23	1.24	1.49	0.466	0.082	0.9884	153	0.065
11	Pluronic F88	−0.63	0.34	1.10	1.60	0.483	0.086	0.9887	153	0.058
	Pluronic F68	−0.66	0.35	1.13	1.61	0.485	0.087	0.9884	154	0.059
	Pluronic F77	−0.63	0.32	1.09	1.61	0.496	0.083	0.9897	151	0.051
	Igepal CO 880	−0.66	0.28	1.16	1.61	0.488	0.084	0.9885	152	0.059
	Triton X 305	−0.83	0.29	1.17	1.65	0.492	0.086	0.9894	154	0.059
12	Ethyleneglycoladipate	−0.90	0.36	1.43	1.72	0.443	0.093	0.9857	143	0.073
	Diethyleneglycoladipate	−0.91	0.40	1.46	1.73	0.438	0.089	0.9847	139	0.065
13	XF-1150	−0.69	0.06	1.44	1.38	0.417	0.084	0.9856	150	0.092
	Sucrose octaacetate	−0.73	0.12	1.48	1.59	0.426	0.090	0.9852	154	0.071
14	Carbowax 20M	−0.73	0.40	1.23	1.78	0.465	0.091	0.9880	153	0.059
	Carbowax 6000	−0.75	0.40	1.28	1.80	0.469	0.090	0.9878	150	0.059
	Carbowax 4000	−0.76	0.32	1.31	1.85	0.470	0.090	0.9867	149	0.059
	Carbowax 1540	−0.75	0.31	1.34	1.87	0.457	0.093	0.9866	151	0.069
	Carbowax 1000	−0.76	0.29	1.37	1.89	0.457	0.094	0.9867	152	0.071

(Continued on p. 336)

TABLE III *(continued)*

Group	Stationary phase	Characteristic constants in eqn. 1					S.D.	R	No	q
		c	r	s	a	l				
15	Carbowax 600	−0.82	0.31	1.46	2.12	0.455	0.093	0.9847	149	0.073
	Carbowax 400	−0.77	0.28	1.50	2.18	0.440	0.090	0.9883	149	0.077
	Carbowax 300	−0.79	0.33	1.50	2.28	0.434	0.093	0.9877	149	0.074
	Quadrol	−0.77	0.07	1.47	2.38	0.471	0.103	0.9858	153	0.087
	Hyprose SP80	−0.87	0.11	1.53	2.40	0.414	0.103	0.9835	151	0.088
16	Triethyleneglycolsuccinate	−1.05	0.39	1.71	1.87	0.416	0.090	0.9858	145	0.078
	Diethyleneglycolsuccinate	−0.99	0.43	1.74	1.68	0.379	0.114	0.9755	145	0.073
	Dow Corning Fluid 550	−0.46	0.09	0.56	0.29	0.547	0.047	0.9963	152	0.032
	Casterwax	−0.45	0.10	0.63	1.09	0.562	0.060	0.9944	150	0.040
	Dibutyltetrachlorophthalate	−0.62	0.25	0.69	0.60	0.600	0.048	0.9969	150	0.038
	Citroflex A4[a]	−0.43	0.12	0.85	0.94	0.552	0.061	0.9951		0.046
	Bis(2-ethoxyethyl)phthalate	−0.64	0.13	1.23	1.25	0.529	0.074	0.9923	152	0.067
	Dow Corning Fluid FS 1265	−0.76	−0.25	1.29	0.29	0.451	0.083	0.9851	153	0.086
	Kroniflex THPP	−0.72	0.22	1.34	2.28	0.498	0.083	0.9913	152	0.071
	Zonyl E-7	−0.82	−0.28	1.63	0.69	0.449	0.071	0.9902	150	0.083

[a] Values extrapolated from 80 and 100 °C.

CHARACTERISATION OF PHASES

Details of the application of eqn. 1 to the 77 McReynolds phases are given in Tables III, IV, VI and VII. In Table III are results at a common temperature of 120°C, with values for squalane and Citroflex A4 extrapolated from those at 80 and 100°C. Table IV contains results at temperatures other than 120°C, usually at 100 or at 140/160°C, so that all of McReynolds data sets have been analysed. We do not list the chemical formulation of the 77 phases, even though some of them are rather obscure, because Fellous *et al.* [6] have detailed the 77 stationary phases already. It should be noted that many of these phases contain a non-ionic surfactant (2%, w/w), and hence our obtained constants, Table III, refer to the phases as specifically formulated by McReynolds [1]. Although many of the McReynolds phases are no longer in current use, we list results for all the phases in order to show the utility of our method and in order to compare our classification with previous characterisation [12] of the total 77-phase set.

Furthermore, no corrections were made by McReynolds for effects such as interfacial adsorption, and his results for solutes such as alkanes in the more polar phases may be subject to additional error. We have no way of correcting the raw data of McReynolds, and rather than exclude particular subsets of compounds on some arbitrary basis, we have chosen to use all the available results. This may well account for part of the large standard deviations observed for regressions with phases such as diglycerol and sorbitol, and suggests also that the obtained constants for these phases should be viewed with some caution.

In principle, a given stationary phase at a given temperature is characterised by the six constants in eqn. 1. However, the constant c, although important as regards the absolute values of log V_G^0, is not a very useful characteristic constant, whilst the constant r plays only a minor role, at least for the present data set. We are thus left with the four constants s, a, b and l. But we can effect further simplication by noting that only three out of the 77 phases give rise to statistically significant b constants, and hence show hydrogen-bond acidity. These are docosanol, diglycerol and sorbitol with b values of 0.34, 0.52 and 0.34 respectively at 120°C (see Table VI). A number of the other phases might be expected to show hydrogen-bond acidity, but the analysis given in Table VIII reveals that the $b\beta_2^H$ term is not significant. We can therefore regard docosanol, diglycerol and sorbitol as singular phases, and analyse the remaining 74 phases with the omission of the $b\beta_2^H$ term altogether (see Tables III and IV). For these 74 phases, the three major characteristic constants are thus s, a and l only.

We begin the analysis of the 74 phases in Table III by noting that there is some connection between s, a and l. In general, basic phases will also be dipolar, so that a and s will tend to run together. Furthermore, solvent–solvent interactions will be greater in dipolar, basic phases, thus giving rise to a larger endoergic cavity term, leading to a smaller value of the l constant. Since a and s are likely to be related, we can first group the 74 phases through a plot of a against s, shown in Fig. 1. Quite clearly, there are several groups or clusters of phases with about the same a and s values, and we have drawn up Table III to show the 16 clusters indicated in Fig. 1. Of course, there is an arbitrary element in the choice of clusters. Thus groups 9 and 11 might be subsumed into a common group, or group 4 might be divided into two groups, but this is a feature of any method that reduces the 77 phases down to a

TABLE IV

REGRESSIONS AT VARIOUS TEMPERATURES

Stationary phase	*c*	*r*	*s*	*a*	*l*	S.D.	*R*	No	Temperature (°C)
Squalane	−0.21	0.11	0.08	–	0.735	0.043	0.9970	133	80
	−0.27	0.12	0.05	–	0.674	0.034	0.9983	147	100
Apiezon M	−0.57	0.28	0.13	0.06	0.504	0.044	0.9971	153	160
Apiezon N	−0.62	0.28	0.15	0.09	0.504	0.045	0.9969	153	160
Apiezon J	−0.62	0.28	0.17	0.11	0.501	0.038	0.9977	150	160
Apiezon L	−0.57	0.29	0.10	0.05	0.502	0.037	0.9975	151	160
Versilube F50	−0.48	0.08	0.22	0.09	0.444	0.037	0.9972	152	160
SE-31	−0.48	0.05	0.22	0.14	0.430	0.038	0.9968	157	160
SE-30	−0.45	0.06	0.23	0.18	0.441	0.036	0.9968	154	160
SE-30 NPGA	−0.50	0.05	0.30	0.28	0.486	0.039	0.9970	139	140
SE-52	−0.51	0.07	0.29	0.17	0.442	0.040	0.9966	157	160
Dioctylsebacate	−0.31	0.13	0.55	0.94	0.646	0.049	0.9969	154	100
Di-2-ethylhexylsebacate	−0.31	0.13	0.55	0.95	0.646	0.050	0.9969	154	100
Tripelargonate	−0.53	0.15	0.49	0.65	0.486	0.051	0.9957	154	160
Isooctyldecyladipate	−0.33	0.11	0.60	0.96	0.645	0.054	0.9964	155	100
Di-2-ethylhexyladipate	−0.31	0.11	0.61	1.04	0.644	0.052	0.9966	152	100
Diisodecylphthalate	−0.55	0.14	0.59	0.62	0.537	0.050	0.9964	156	140
Dioctylphthalate	−0.55	0.15	0.61	0.64	0.532	0.052	0.9960	155	140
Ucon LB-1715	−0.69	0.20	0.61	0.88	0.459	0.061	0.9924	152	160
Flexol 8N8	−0.54	0.07	0.69	1.09	0.524	0.057	0.9953	157	140
Pluronic L81	−0.44	0.18	0.84	1.56	0.589	0.081	0.9910	151	100
Polyphenyl ether, 5 rings	−0.86	0.23	0.82	0.44	0.482	0.060	0.9936	156	160
Polyphenyl ether, 6 rings	−0.87	0.24	0.82	0.46	0.478	0.063	0.9929	156	160
Tricresylphosphate	−0.62	0.15	1.14	1.44	0.600	0.078	0.9920	142	100
Sucrose acetate isobutanoate	−0.65	0.06	0.86	0.99	0.429	0.060	0.9925	155	160
Hallcomid M18	−0.31	0.11	0.65	1.89	0.649	0.066	0.9943	141	100
Hallcomid M180L	−0.38	0.10	0.74	1.90	0.646	0.069	0.9934	141	100

Pluronic L42	−0.59	0.20	0.82	1.26	0.486	0.074	0.9902	155	140
Pluronic L72	−0.61	0.23	0.81	1.23	0.489	0.072	0.9917	155	140
Pluronic L61	−0.50	0.21	1.02	1.67	0.581	0.088	0.9890	141	100
Pluronic L63	−0.47	0.17	1.01	1.71	0.571	0.083	0.9890	140	100
Polytergent J300	−0.49	0.15	1.01	1.76	0.584	0.089	0.9901	155	100
Pluronic P84	−0.52	0.25	1.00	1.70	0.564	0.090	0.9893	153	100
Pluronic P85	−0.52	0.27	1.03	1.71	0.562	0.091	0.9892	154	100
Pluronic L44	−0.62	0.25	0.89	1.31	0.473	0.078	0.9899	155	140
Oronite NIW	−0.81	0.20	0.90	1.12	0.458	0.071	0.9906	154	160
Ucon HB-2000	−0.52	0.29	1.03	1.67	0.560	0.094	0.9884	153	100
Ethofat 60-25	−0.57	0.19	1.08	1.78	0.575	0.086	0.9909	151	100
Pluronic P65	−0.50	0.27	1.05	1.76	0.560	0.090	0.9881	143	100
Pluronic P46	−0.46	0.30	0.94	1.38	0.466	0.079	0.9893	156	140
Tergitol NPX	−0.66	0.24	0.86	1.13	0.437	0.066	0.9916	152	160
Neopentylglycoladipate, term	−0.76	0.16	1.03	1.31	0.475	0.065	0.9928	140	140
Ethyleneglycolsebacate	−0.81	0.22	1.02	1.32	0.478	0.067	0.9930	132	140
Diethyleneglycolsebacate	−0.83	0.27	1.06	1.34	0.460	0.073	0.9909	136	140
Neopentylglycoladipate	−0.67	0.18	1.02	1.32	0.444	0.064	0.9926	140	140
Neopentylglycolsuccinate	−0.72	0.16	1.15	1.39	0.418	0.070	0.9905	139	140
Pluronic F88	−0.58	0.28	1.21	1.83	0.531	0.095	0.9878	153	100
Pluronic F68	−0.60	0.29	1.24	1.81	0.530	0.098	0.9878	156	100
Pluronic F77	−0.57	0.32	1.19	1.87	0.547	0.094	0.9871	141	100
Igepal CO 880	−0.66	0.27	1.28	1.88	0.540	0.096	0.9890	152	100
Triton X 305	−0.86	0.31	0.94	1.26	0.407	0.072	0.9890	152	160
Ethyleneglycoladipate	−0.97	0.24	1.37	1.68	0.412	0.083	0.9868	129	140
Diethyleneglycoladipate	−0.92	0.30	1.34	1.61	0.399	0.079	0.9865	130	140
XF-1150	−0.82	0.06	1.30	1.12	0.344	0.076	0.9843	152	160
Sucrose octaacetate	−0.84	0.12	1.29	1.30	0.362	0.076	0.9852	154	160
Carbowax 20M	−0.82	0.37	1.07	1.36	0.392	0.076	0.9879	151	160
Carbowax 6000	−0.79	0.40	1.15	1.56	0.431	0.083	0.9877	152	140
Carbowax 4000	−0.81	0.37	1.18	1.64	0.431	0.080	0.9889	150	140
Carbowax 1540	−0.71	0.38	1.42	2.17	0.499	0.100	0.9874	150	100
Carbowax 1000	−0.73	0.30	1.49	2.24	0.500	0.100	0.9875	149	100

(Continued on p. 340)

TABLE IV *(continued)*

Stationary phase	*c*	*r*	*s*	*a*	*l*	S.D.	*R*	No	Temperature (°C)
Carbowax 600	−0.78	0.29	1.61	2.39	0.496	0.104	0.9866	148	100
Carbowax 400	−0.73	0.28	1.60	2.44	0.481	0.104	0.9867	150	100
Carbowax 300	−0.76	0.26	1.64	2.56	0.476	0.106	0.9866	149	100
Quadrol	−0.72	0.12	1.50	2.76	0.521	0.106	0.9879	152	100
Hyprose SP80	−0.84	0.09	1.61	2.77	0.461	0.110	0.9848	150	100
Triethyleneglycolsuccinate	−1.06	0.33	1.57	1.67	0.381	0.086	0.9840	133	140
Diethyleneglycolsuccinate	−1.07	0.35	1.60	1.77	0.342	0.099	0.9746	133	140
Dow Corning Fluid 550	−0.56	0.11	0.47	0.20	0.456	0.041	0.9967	154	160
Casterwax	−0.56	0.13	0.60	0.93	0.519	0.053	0.9953	152	140
Dibutyltetrachlorophthalate	−0.57	0.24	0.75	0.68	0.658	0.057	0.9956	142	100
Citroflex A4	−0.29	−0.06	1.05	1.47	0.658	0.072	0.9923	136	80
	−0.36	0.04	0.94	1.19	0.602	0.066	0.9938	150	100
Bis(2-ethoxyethyl)phthalate	−0.58	0.18	1.29	1.46	0.575	0.085	0.9899	143	100
Dow Corning Fluid FS 1265	−0.86	−0.21	1.13	0.27	0.367	0.071	0.9853	155	160
Kroniflex THFP	−0.79	0.23	1.25	2.02	0.461	0.082	0.9901	153	140
Zonyl E-7	−0.78	−0.29	1.78	0.78	0.494	0.077	0.9905	138	100

TABLE V

CHARACTERISATION OF PHASES USING EQN. 1 WITH McREYNOLD'S AND LAFFORT'S DATA AT 120 °C

M = McReynold's set, this work; L = Laffort's set, ref. 16.

Stationary phase	Set	*r*	*s*	*a*	*l*
Carbowax 1540	M	0.31	1.34	1.87	0.457
	L	0.26	1.37	2.11	0.442
Diethyleneglycolsuccinate	M	0.43	1.74	1.68	0.379
	L	0.35	1.70	1.92	0.396
Polyphenyl ether, 6 rings	M	0.21	0.90	0.56	0.563
	L	0.19	0.98	0.59	0.552
Zonyl E-7	M	−0.28	1.63	0.69	0.449
	L	−0.38	1.61	0.70	0.442

TABLE VI

STATIONARY PHASES WITH SIGNIFICANT HYDROGEN-BOND ACIDITY

Stationary phase	*c*	*r*	*s*	*a*	*b*	*l*	S.D.	*R*	No	Temperature (°C)
Docosanol[a]	−0.41	0.13	0.29	0.75	0.34	0.603	–	–	–	120
	−0.37	0.15	0.30	1.13	0.39	0.657	0.061	0.9951	148	100
	−0.33	0.16	0.31	1.56	0.45	0.717	0.077	0.9925	134	80
Diglycerol	−1.26	0.55	1.63	2.77	0.52	0.225	0.148	0.9589	146	120
Sorbitol	−1.72	0.35	0.81	1.77	0.34	0.360	0.161	0.9217	130	120

[a] Extrapolated from results at 80 and 100 °C.

TABLE VII

TEST FOR STATIONARY PHASE HYDROGEN-BOND ACIDITY

Stationary phase	*c*	*r*	*s*	*a*	*b*	*l*	S.D.	*R*
Castorwax	−0.47	0.13	0.59	1.06	0.08	0.563	0.059	0.9945
	−0.45	0.10	0.63	1.09	–	0.562	0.060	0.9944
Flexol 8N8	−0.49	0.12	0.71	1.25	0.03	0.573	0.065	0.9932
	−0.48	0.11	0.73	1.27	–	0.573	0.065	0.9932
Hyprose SP80	−0.86	0.09	1.56	2.42	0.05	0.414	0.103	0.9835
	−0.87	0.11	1.53	2.40	–	0.414	0.103	0.9835
Quadrol	−0.77	0.08	1.45	2.37	0.03	0.472	0.103	0.9858
	−0.77	0.07	1.47	2.38	–	0.471	0.103	0.9858

TABLE VIII

EFFECT OF CHAIN LENGTH ON THE CHARACTERISTIC CONSTANTS FOR SOME STATIONARY PHASE ESTERS

Stationary phase	*r*	*s*	*a*	*l*
Dioctylsebacate	0.12	0.49	0.79	0.594
Ethyleneglycolsebacate	0.27	1.10	1.44	0.518
Diethyleneglycolsebacate	0.32	1.14	1.45	0.498
Isooctyldecyladipate	0.13	0.55	0.81	0.586
Ethyleneglycoladipate	0.36	1.43	1.72	0.443
Diethyleneglycoladipate	0.40	1.46	1.73	0.438
Diethyleneglycolsebacate	0.32	1.14	1.45	0.498
Diethyleneglycoladipate	0.40	1.46	1.73	0.438
Diethyleneglycolsuccinate	0.43	1.74	1.68	0.379

relatively small number of clusters. We can then examine the 16 groups to see if any futher subdivision is necessary on the basis of the *r* and *l* constants. However, within each group, the *r* and *l* constants do not vary overmuch. Only in the case of group 7 and group 16 is there a clear subdivision into high and low values of *l*, although groups 10 and 15 do contain a rather wide spread of *l* values.

We can conclude that an analysis in terms of *s* and *a* (and also *b* for phases that are hydrogen-bond acids) enables us to group the 74 McReynolds phases into a number of clusters of similar phases, leaving some 11 stationary phases (8 in Table III plus the three acidic phases) as singular phases that cannot be substituted by any other of the 77-phase set. Our grouping is based entirely on chemical principles, and it

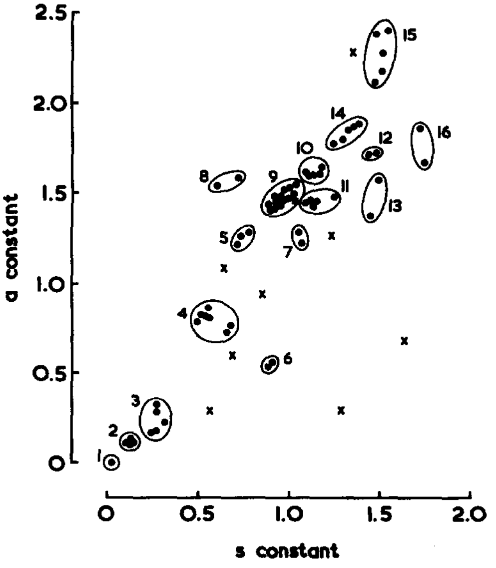

Fig. 1. Classification of stationary phases according to the *a* constant and the *s* constant in eqn. 1. ● = Groups as shown in Table III; × = singular phases.

is very instructive to compare results with other work carried out on more mathematical lines.

Huber and Reich [12] have analysed the 77-phase set, using both hierarchical clustering and the minimum spanning tree method. Their results, especially by the latter technique, are almost identical to those we have obtained. Differences, such as there are, are trivial. For example Huber and Reich [12] class Castorwax and our groups 5 and 8 together, but reference to Table III and Fig. 1 shows that this is quite reasonable on our analysis as well. Wold [11] used a pattern cognition method to group the 226-phase set into clusters. Where there are common phases between the 226- and the 77-phase sets, there is again excellent agreement between our result and those of Wold [11]. As pointed out by Wold, the nearest neighbour technique used by Leary *et al.* [7] leads to a rather peculiar set of clusters. However, the numerical taxonomy method of Massart *et al.* [9] applied to the 226-phase set leads to groups not too dissimilar to those in Table III, although there are some outstanding exceptions. Thus Massart *et al.* [9] class didecylphthalate and Flexol 8N8 in the same group, whereas we find the latter to be considerably more basic ($a = 1.27$ as against $a = 0.73$ for diisodecylphthalate). Our method of clustering, therefore, is in excellent agreement with results of Huber and Reich [12] and of Wold [11], but not so much with results of Leary *et al.* [7] or of Massart *et al.* [9].

A general survey of our classification, Table III, shows that it is completely consistent with the chemical formulation of the phases. Thus group 1 contains the saturated hydrocarbon squalane, and would include other hydrocarbons such as hexadecane (by definition), octacosane, $C_{87}H_{176}$ etc. The apiezons in group 2 are slightly dipolar and basic due to the presence of some aromatic groups, whilst the silicones in group 3 are rather more dipolar and basic through the silicon–oxygen bond. Thus the hydrogen-bond basicity of $(CH_3)_3SiOSi(CH_3)_3$ as a solute, $\beta_2^H = 0.16$, can be compared to values of β_2^H for di-*tert.*-butylether of 0.38, and values of around 0.45 for straight-chain aliphatic ethers [22]. All the simple esters of carboxylic acids cluster in group 4, the two amides appear in group 8, and so forth. The Carbowaxes fall into an exact sequence from Carbowax 20M to Carbowax 300, with values of s and a monotonically increasing along the series, where the cut-off point between groups 14 and 15 is clearly arbitrary. The sebacates (C_{10}), adipates (C_6) and succinates (C_4) are worthy of attention (see Table VIII). The sebacates are always less dipolar and less basic than the adipates or succinates, and the simple dialkylesters are always less dipolar and less basic than the corresponding ethyleneglycol or diethyleneglycol ester.

The constant r does not vary widely over the particular set of 77 phases, but, significantly, the r constant is negative in the case of the only fluorinated stationary phases in the set, *viz.* Dow Corning Fluid FS 1265 and Zonyl E-7. The ability of these phases to interact with solute π- and n-electron pairs is even less than that of a simple alkane.

Finally, we consider the characteristic constant l, a resultant of an endoergic solvent cavity term tending to decrease the value of l and an exoergic general dispersion interaction term tending to increase the value of l. We have previously shown [16] that the methylene increment for solvation of a homologous series[a] of gaseous

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[a] That is a series in which CH_2 groups are successively inserted at the same part of the molecule.

TABLE IX

VALUES OF ΔLOG V_G^0 FOR 1-ALKANOLS ON SOME STATIONARY PHASES

R and No = Correlation coefficients and number of points in plots of log V_G^0 against carbon number of the 1-alkanols.

Stationary phase	Temperature (°C)	*l*	Δlog V_G^0	*R*	No
Squalane	80	0.735	0.398	0.9991	5
Squalane	100	0.674	0.358	0.9988	7
Squalane[a]	120	0.619	0.322	–	–
Apiezon N	120	0.601	0.314	0.9993	7
SE-30	120	0.523	0.280	0.9996	7
Carbowax 400	120	0.440	0.235	0.9998	7
Diethyleneglycolsuccinate	120	0.379	0.198	0.9989	7
Diglycerol	120	0.225	0.110	0.9987	7

[a] Extrapolated values.

solutes in a given solvent, $\Delta G_s^0(CH_2)$, depends on a combination of a solvent cavity term and a general dispersion interaction term. Now $\Delta G_s^0(CH_2)$ is related to Δlog V_G^0, since $\Delta G_s^0(CH_2) = -2.303RT\Delta\log V_G^0$, where Δlog V_G^0, is the average increase in log V_G^0, along an homologous series. It therefore follows that the constant *l* must also be related to the important term Δlog V_G^0, or $\Delta G_s^0(CH_2)$.

In Table IX are given values of Δlog V_G^0, for the homologous series of l-alkanols in a few representative stationary phases covering the range of *l* constants we have encountered. A plot of Δlog V_G^0, against the *l* constant (Fig. 2) yields an excellent straight line passing through the origin, since Δlog V_G^0 must approach zero as *l* approaches zero. We can thus show from experiment, as well as theory, that the *l* constant in eqn. 1 is a measure of the ability of a stationary phase to separate mem-

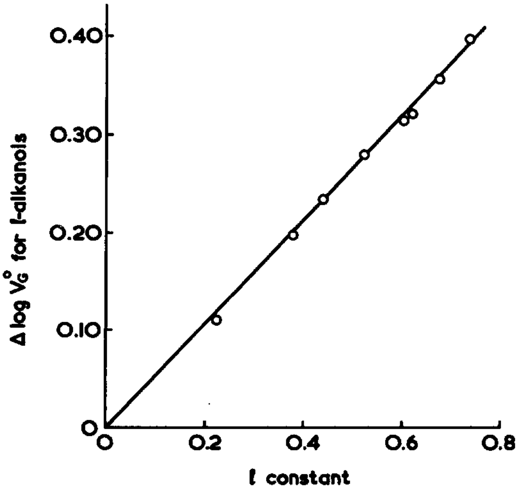

Fig. 2. Plot of Δlog V_G^0 against the *l* constant.

TABLE X

CHARACTERISTIC CONSTANTS FOR OTHER PHASES AT 120°C

Phase	*r*	*s*	*a*	*l*
N-methylpyrrolidinone [17]	–	1.42	2.70	0.472
N-Formylmorpholine [17]	–	1.52	2.24	0.442
Tricyanoethoxypropane [16]	0.23	2.12	1.94	0.379

bers of an homologous series. The *l* constant is entirely equivalent to $\Delta G_s^0(CH_2)$, so that eqn. 1 actually incorporates this latter parameter.

We have not considered eqns. 2 and 3 other than to compare them with eqn. 1 in Table II. Eqn. 2 offers no advantage over eqn. 1 and suffers from the disadvantage of containing the empirical parameter δ_2. Eqn. 3, although giving rise to significantly worse fits than eqn. 1 has the advantage that the *q* constant, especially, can be related to a theoretical model of solute dipole–solvent interactions via the Kirkwood equation [27]. However, in practice the correlation constant between *q* and *s* is so high, 0.970 for the 77 stationary phases at 120°C, that no extra information is contained in *q*. At present, therefore, eqn. 3 is not necessary for the characterisation of stationary phases. However, the dipole moment term is theoretically very useful, and it might be possible to incorporate other solute parameters, and to obtain an improved version of eqn. 3 that retains the dipole moment as a dipolarity parameter.

In Table X we list a few phases that we have previously [16,17] characterised through eqn. 1. The two amides are highly basic, whilst tricyanoethoxypropane is the most dipolar phase we have examined to data. Finally, we give in Table XI a selection of phases to show how the characteristic constants *s*, *a*, *b* and *l* relate to the chemical

TABLE XI

CHEMICAL CHARACTERISTICS OF SOME PHASES

Phase	Polarity	Basicity	Acidity	Separation of homologues
Hexadecane Squalane	Zero	Zero	Zero	High
Apiezon	Low	Low	Zero	High
Polyphenylether	Medium	Low	Zero	High
Hallcomid Kroniflex THFP	Medium	High	Zero	Medium
Carbowax 300 Quadrol Hyprose SP80	High	High	Zero	Medium
Zonyl E-7	High	Low	Zero	Medium
N-Methylpyrrolidinone	High	Very high	Zero	Medium
Tricyanoethoxypropane	Very high	High	Zero	Low
Docosanol	Low	Medium	Low	High
Diglycerol	High	Very high	Medium	Very low

nature of the stationary phase. From such a list, it is easy to select a phase that will effect separations mainly through dipole–dipole interactions (*e.g.* Zonyl E-7), or a phase that will effect separations mainly through interactions of the type solute hydrogen-bond acid–solvent hydrogen-bond base (e.g. Hallcomid M18 or M180L). We have not been able to list any phase that leads mainly to interactions of the type solute hydrogen-bond base–solvent hydrogen-bond acid. The most acidic phase we have encountered is diglycerol with b = 0.52 at 120°C, but this phase is actually the strongest hydrogen-bond base of all the phases listed. In any case, diglycerol is unsuitable as a general stationary phase because of the very low l constant. We hope to report in the near future on our attempts to synthesise phases that are strong hydrogen-bond acids but weak hydrogen-bond bases.

In conclusion, we have been able to set up a new classification of stationary phases, based on fundamental chemical interactions. The characteristic constants r, s, a, b and l provide information on the propensity of a given phase to undergo specific interactions with solutes, and hence lead to criteria for the choice of a phase to effect particular separations. The method does not have the disadvantages of the McReynolds–Rohrschneider procedures, and although retention data on not less than about 25 solutes are required, it is necessary only to determine relative retention times. Another advantage of the present method is that eqn. 1 can be applied to equilibria involving any condensed phase, for example the solubility of gaseous solutes in simple organic solvents [17], or even the adsorption of gases on solids. We hope to report on these processes in the near future.

SOLUTE–SOLVENT INTERACTIONS

Our main aim in this paper has been to characterise the set of 77 McReynolds phases in terms of eqn. 1, where SP = V_G^0. However, we can now use the results given in Tables III–VI to analyse the factors that influence solute retention on stationary phases. We give in Table XII a breakdown of eqn. 1, term-by-term for two typical solutes, butanone and 1-butanol, in a variety of stationary phases. In the less polar

TABLE XII

ANALYSIS OF THE FACTORS THAT INFLUENCE LOG V_G^0, USING EQN. 1 AT 120°C

Solute	Phase	Term					Dispersion[a]	Cavity[a]
		rR_2	$s\pi_2^*$	$a\alpha_2^H$	$b\beta_2^H$	$l \log L^{16}$		
Butanone	Apiezon M	0.04	0.07	0	0	1.37	3.36	−1.93
	Hallcomid M18	0.02	0.40	0	0	1.35	3.26	−1.88
	Zonyl E-7	−0.05	1.09	0	0	1.03	1.90	−1.09
	Diglycerol	0.09	1.09	0	0.25	0.52	(0.48)	(−0.28)
1-Butanol	Apiezon M	0.06	0.40	0.04	0	1.56	4.10	−2.25
	Hallcomid M18	0.03	0.24	0.52	0	1.54	4.00	−2.20
	Zonyl E-7	−0.06	0.65	0.23	0	1.17	2.31	−1.27
	Diglycerol	0.12	0.65	0.91	0.23	0.59	(0.59)	(−0.32)

[a] See text. These do not add up to the $l \log L^{16}$ term because of a constant term and a small dipole–induced dipole term that have not been included.

phases, where the s constant is quite small, by far the main term is $l \log L^{16}$. The term $a\alpha_2^H$ can be substantial for the combination of a hydrogen-bond acidic solute and a hydrogen-bond basic phase, but for the present set of solutes and phases the $b\beta_2^H$ term is never substantial. Of course, for more acidic phases than diglycerol, the $b\beta_2^H$ term could be much more significant.

In eqn. 1, the $l \log L^{16}$ term covers both general dispersion interactions that lead to positive values of $\log V_G^0$, and the endoergic solvent–solvent cavity term that leads to negative values of $\log V_G^0$. These two effects are very difficult to unravel quantitatively, hence we have had to use a combined term in eqn. 1. Abraham and Fuchs [24], however, managed to dissect the $\log L^{16}$ values themselves into mainly a cavity term and a general dispersion interaction term. If we assume, as before [25], that the ratio of these two terms remains the same, then we can roughly separate the total $l \log L^{16}$ term shown in Table XII into cavity and general dispersion effects. Given that these are only approximations, expecially in the case of diglycerol, we can still see that the largest interaction term corresponds to general solute–solvent dispersion effects. It is these that control the separation of members of an homologous series. Eqn. 1 incorporates such an effect in the $l \log L^{16}$ term. Although dipolar and acid–base interactions tend to be smaller than the general dispersion interactions, they control separations of dissimilar solutes. Eqn. 1 incorporates these effects in the first four terms.

Thus our preferred eqn. 1 not only forms the basis of a classification of stationary phases, but also leads to a rationale for the separation of solutes, based on a number of possible solute–solvent interactions.

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