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Hydrogen bonding

XVII. The characterisation of 24 gas–liquid chromatographic stationary phases studied by Poole and co-workers, including molten salts, and evaluation of solute–stationary phase interactions

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ABSTRACT

The general solvation equation

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

has been used to characterise 24 gas–liquid chromatographic stationary phases for which Poole and co-workers have determined log K values for a series of solutes at 121.4°C. The explanatory variables are R_2, a solute excess molar refraction, π_2^H, the solute dipolarity, α_2^H and β_2^H, the solute hydrogen-bond acidity and basicity, and log L^{16}, where L^{16} is the solute gas–liquid partition coefficient on hexadecane at 25°C. It is shown that the $b\beta_2^H$ term is not significant for any phase, and that the molten salts are all strongly dipolar and basic, with large s and a constants. A term-by-term analysis of the solvation equation yields a quantitative measure of the contribution to log K of various solute–stationary phase interactions, and leads to an understanding of how these interactions affect solute retention. The use of the characteristic constants c, r, s, a, b and l in the selection of stationary phases for particular separations is described.

INTRODUCTION

There have been a number of interesting new developments in recent years in the characterisation of gas–liquid chromatographic (GLC) stationary phases. Poole and co-workers [1,2] have pointed out several deficiences in the McReynolds system of classification, and have suggested that the use of McReynolds numbers be abandoned. Following several other workers [3–5], Poole and co-workers suggested that the Gibbs energy of solvation of a gaseous methylene increment into a stationary phase, $\Delta G_s^0(CH_2)$, could be used as a measure of the "polarity" of the phase [1,2,6]. More recently, Poole and co-workers [7,8] defined a solvent strength parameter, *SSP*, as $SSP = \Delta G_s^0(CH_2)/\rho_1$, where ρ_1 is the density of the stationary phase at the column temperature. Although $\Delta G_s^0(CH_2)$, or alternatively *SSP*, might well be the best "single parameter" that can be used to classify stationary phases, it cannot possibly reflect the various solute–solvent interactions that determine the retention of a solute by a given stationary phase. The use of various test solutes as probes cannot be used to identify such interactions either, because there are no test solutes that possess, for example, a singular quality of "polarity" without also possessing some other quality. Thus a test solute such as 1-nitropropane, although certainly dipolar, is also basic, whereas a test solute such as butan-1-ol is acidic, basic and dipolar! Poole and co-workers [2,7,8] recognised this difficulty, although no easy solution to the problem seemed to be available.

In parallel with these studies, we have been developing the use of equations based on multiple linear regression analysis (MLRA) in order to identify and to quantify solute–solvent interactions as a means of classifying stationary phases. Our recommended solvation equation is

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

where *SP* can be the retention volume at the column temperature, the specific retention volume, the gas–liquid partition coefficient (*L* or *K*) or even the retention time or relative retention time corrected for gas hold-up, for a series of solutes on a given stationary phase [9–11]. All these quantities will yield the same characteristic constants *r*, *s*, *a*, *b* and *l*. Note that the retention index, *I*, cannot be used in eqn. 1 unless the alkane *b* values are also given. It is to be hoped that when *I* values are tabulated, workers will also include data that will enable the original retention values to be calculated.

The explanatory variables in eqn. 1 are solute properties as follows: R_2 is an excess molar refraction [9], π_2^H is our new solute dipolarity–polarisability parameter [12], α_2^H is the effective or summation hydrogen-bond acidity that could be denoted $\Sigma\alpha_2^H$ [12], β_2^H is the effective or summation hydrogen-bond basicity that could be denoted $\Sigma\beta_2^H$ [12] and L^{16} is the solute *L* or *K* value on *n*-hexadecane at 25°C [13]. Of course, most $\log L^{16}$ values have now been determined via back-calculation of retention data on various non-polar phases. The constants in eqn. 1 are found by MLRA, using log *SP* values for a series of varied solutes on a given stationary phase. As *r*, *s*, *a*, *b* and *l* quantitatively relate to stationary phase properties, they are denoted as "characteristic constants". In particular, the *r* constant refers to the ability of the phase to interact with solute π- and *n*-electron pairs, the *s* constant refers to the ability of the phase to take part in dipole–dipole and dipole–induced dipole interactions, the *a* constant refers to the interaction of the phase with solute hydrogen-bond acids and hence is a measure of the hydrogen-bond basicity of the phase, the *b* constant likewise measures the hydrogen-bond acidity of the phase and the *l* constant refers to the ability of the phase to separate adjacent members of a homologous series. The *l* constant should therefore be connected with $\Delta G_s^0(CH_2)$, because the larger is *l* or $\Delta G_s^0(CH_2)$ the greater will be the separation between adjacent homologues [11].

We have already shown how eqn. 1 can be used to characterise stationary phases in the McReynolds and Patte *et al.* series [9,11] and how retention data in these two series may then be used to obtain π_2^H and α_2^H solute parameters [12]. As these two activities are interdependent, it seems obligatory to test eqn. 1 with an independent set of retention data. We have chosen as a first test the retention data, as log *K* values, obtained by Poole and co-workers [7] on 24 stationary phases at 121.4°C. There are two main reasons for this choice. First, we believe the data obtained by Poole and co-workers [7] to be amongst the most reliable GLC data ever reported, with considerable care being taken to exclude contributions from interfacial adsorption. Second, the stationary phases studied by Poole and co-workers include seven molten salts, and it is of interest to analyse results on these novel stationary phases using the general solvation eqn. 1.

The stationary phases used by Poole and co-workers are shown in Table I, together with their $\Delta G_s^0(CH_2)$ and *SSP* values [7]. Solute parameters were all taken from our previous compilation [12]; for convenience they are set out in Table II.

Note that not all solutes were examined on all phases, so that for any particular phase the number of solutes studied (No.) is less than 42. When we first applied eqn. 1 to Poole and co-workers' data

TABLE I

STATIONARY PHASES EXAMINED BY POOLE AND CO-WORKERS AT 121.4°C

Code	Stationary phase	$\Delta G_s^0(\mathrm{CH_2})$ (cal $\mathrm{mol^{-1}}$)	SSP
A	Squalane	−530	−728
B	SE-30	−463	−578
C	OV-3	−458	−523
D	OV-7	−467	−504
E	OV-11	−475	−478
F	OV-17	−470	−463
G	OV-22	−458	−439
H	OV-25	−431	−396
I	OV-105, poly(cyanopropylmethyldimethylsiloxane)	−461	−523
J	OV-225, poly(cyanopropylmethylphenylmethylsiloxane)	−418	−410
K	OV-275, poly(dicyanoallylsiloxane)	−265	−243
L	OV-330, a poly(dimethylsiloxane)–Carbowax copolymer	−418	−407
M	Poly(trifluoropropylmethylsiloxane), QF-1	−393	−337
O	Carbowax 20M	−400	−387
P	Poly(diethylene glycol succinate), DEGS	−324	−275
Q	1,2,3-Tris(2-cyanoethoxy)propane, TCEP	−280	−273
R	Poly(phenyl ether), five rings, PPE-5	−487	−436
S	Tetraethylammonium 4-toluenesulphonate	−286	−267
T	Tributylammonium 4-toluenesulphonate	−384	−384
U	Tetrabutylammonium 4-toluenesulphonate	−377	−377
V	Tetrabutylammonium picrate	−411	−381
W	Tetrabutylammonium methanesulphonate	−398	−406
X	Tetrabutylammonium N-(2-acetamido)-2-aminoethanesulphonate	−319	−312
Y	Tetrabutylammonium 3-[tris(hydroxymethyl)methylamino]-2-hydroxy-1-propanesulphonate	−290	−276

set, we noted that one of their solutes, oct-1-yne, was always out of line, and consistently behaved in a manner we expected of oct-2-yne. It was subsequently confirmed that the compound listed as oct-1-yne in their data set was indeed oct-2-yne [14]; hence in Table II we list oct-2-yne.

For each stationary phase, we analysed results using exactly the solutes studied by Poole and co-workers [7]. Of the 24 phases with an average of 35 solutes each, we excluded one data point only. The result for 2,6-dimethylaniline on phase V was out of line by over four standard deviations, with log K (obs.) = 2.947 and log K (calc.) = 3.416 units.

RESULTS AND DISCUSSION

As a necessary preliminary, we applied the full eqn. 1 to all 24 phases, and found that in no case was the b coefficient statistically significant as judged by the t-test. We can then revert to the simpler equation,

$$\log K = c + r\mathrm{R}_2 + s\pi_2^{\mathrm{H}} + a\alpha_2^{\mathrm{H}} + l \log L^{16} \qquad (2)$$

Results of application of eqn. 2 to all 24 phases are summarised in Table III, where we give the characteristic constants in eqn. 2, together with the overall standard deviation in log K, (S.D.), the overall correlation coefficient (R) and the number of data points or solutes in each regression (No.).

As judged by the values of S.D. and R, the regression equations for the 24 phases are of excellent quality. Most values of S.D. are <0.08 log unit, and for the four phases with S.D. >0.08, *viz.*, P. U. W and X, the errors in log K quoted by Poole and co-workers [7] are much larger than for the other phases. We can therefore conclude that the solvation parameters that we obtained previously, can, indeed, be used to characterise other GLC stationary phases. Whether such characterisation is useful or not will depend at least in part on whether the characteristic constants r, s, a and l in eqn. 2 make general chemical sense.

TABLE II

SOLUTE PARAMETERS USED IN REGRESSION EQN. 2

Solute	R_2	π_2^H	$\Sigma\alpha_2^H$	Log L^{16}
Heptane	0.000	0.00	0.00	3.173
Octane	0.000	0.00	0.00	3.677
Nonane	0.000	0.00	0.00	4.182
Decane	0.000	0.00	0.00	4.686
Undecane	0.000	0.00	0.00	5.191
Dodecane	0.000	0.00	0.00	5.696
Tridecane	0.000	0.00	0.00	6.200
Tetradecane	0.000	0.00	0.00	6.705
Pentadecane	0.000	0.00	0.00	7.209
Hexadecane	0.000	0.00	0.00	7.714
Butanone	0.166	0.70	0.00	2.287
Pentan-2-one	0.143	0.68	0.00	2.755
Hexan-2-one	0.136	0.68	0.00	3.262
Heptan-2-one	0.123	0.68	0.00	3.760
Octan-2-one	0.108	0.68	0.00	4.257
Nonan-2-one	0.119	0.68	0.00	4.735
Benzene	0.610	0.52	0.00	2.803
Butylbenzene	0.600	0.52	0.00	4.686
cis-Hydrindane	0.439	0.20	0.00	4.610
Oct-2-yne	0.225	0.30	0.00	3.850
Dodec-1-yne	0.133	0.23	0.13	5.657
Butan-1-ol	0.224	0.42	0.37	2.601
2-Methylpentan-2-ol	0.169	0.30	0.31	3.081
Dodecafluoroheptan-1-ol	−0.640	0.55	0.60	3.089
Octan-1-ol	0.199	0.42	0.37	4.619
Phenol	0.805	0.88	0.60	3.897
2,4,6-Trimethylphenol	0.860	0.83	0.37	5.185
Benzonitrile	0.742	1.07	0.00	4.004
1-Nitropropane	0.242	0.95	0.02	2.894
1-Nitropentane	0.210	0.95	0.00	3.938
Nitrobenzene	0.871	1.10	0.00	4.511
1,1,1,2-Tetrachlorethane	0.542	0.63	0.10	3.641
Pyridine	0.631	0.82	0.00	3.003
2,4,6-Trimethylpyridine	0.634	0.72	0.00	4.200
Aniline	0.955	0.96	0.26	3.993
N-Methylaniline	0.948	0.94	0.17	4.494
N,N-Dimethylaniline	0.957	0.82	0.00	4.754
2,6-Dimethylaniline	0.967	0.93	0.20	5.037
1,4-Dioxane	0.329	0.75	0.00	2.892
Methylphenyl ether	0.708	0.73	0.00	3.859
Di-*n*-hexyl ether	0.000	0.25	0.00	5.938
Benzodioxane	0.874	1.01	0.00	4.985
Nonanal	0.150	0.65	0.00	4.900

The rR_2 term generally makes only a minor contribution, but nevertheless the r constant seems well behaved. Phases with a substantial proportion of phenyl groups lead to an increase in the r constant, as expected if this is an index of π- and n-electron pair interaction. Thus, along the OV series of poly (methylphenylsiloxane), the r constant increases as the percentage of phenyl groups increases. The only substantially negative value of the r constant, with phase M, corresponds to the only phase that contains fluorine, again as expected.

More important is the $s\pi_2^H$ term, in which the s constant reflects dipole–dipole and dipole–induced dipole interactions, and so may be taken as a mea-

TABLE III

REGRESSION EQUATIONS FOR THE PHASES IN TABLE I

Code	*c*	*r*	*s*	*a*	*l*	S.D.	*R*	No.
A	−0.202	0.125	0.018	−0.097	0.581	0.033	0.9985	39
B	−0.194	0.024	0.190	0.125	0.498	0.022	0.9989	39
C	−0.181	0.033	0.328	0.152	0.503	0.021	0.9992	39
D	−0.231	0.056	0.433	0.165	0.510	0.025	0.9989	39
E	−0.303	0.097	0.544	0.174	0.516	0.029	0.9985	39
F	−0.326	0.128	0.612	0.147	0.509	0.036	0.9978	38
G	−0.328	0.201	0.664	0.190	0.489	0.034	0.9979	38
H	−0.273	0.277	0.644	0.182	0.472	0.042	0.9973	39
I	−0.212	−0.038	0.395	0.368	0.499	0.026	0.9987	39
J	−0.509	0.015	1.214	0.964	0.462	0.035	0.9979	39
K	−0.635	0.388	1.902	1.644	0.241	0.080	0.9935	32
L	−0.430	0.104	1.056	1.419	0.481	0.051	0.9954	36
M	−0.251	−0.362	1.101	0.054	0.416	0.077	0.9853	39
O	−0.558	0.285	1.292	1.803	0.450	0.059	0.9957	39
P	−0.498	0.351	1.683	1.718	0.311	0.096	0.9899	38
Q	−0.489	0.278	1.913	1.679	0.290	0.056	0.9972	40
R	−0.395	0.230	0.829	0.337	0.527	0.044	0.9972	39
S	−1.008	0.362	2.059	3.609	0.340	0.076	0.9941	29
T	−0.717	0.110	1.546	2.917	0.466	0.069	0.9922	30
U	−0.617	0.009	1.659	3.360	0.440	0.106	0.9885	34
V	−0.542	0.100	1.557	1.424	0.445	0.061	0.9935	36[a]
W	−0.631	0.095	1.595	3.408	0.437	0.097	0.9895	34
X	−0.666	0.283	1.809	3.417	0.329	0.100	0.9902	34
Y	−0.690	0.281	1.821	2.859	0.305	0.080	0.9932	29

[a] Excluding solute 2,6-dimethylanilline, which is out of line by over four standard devations; log *K* (calc.) = 3.416, log *K* (obs.) = 2.947

sure of stationary phase dipolarity. Of the conventional phases, phases K (OV-275), P (DEGS) and Q (TCEP) have the largest *s* constants of *ca.* 1.7–1.9 units. The ionic salts (S–Y) all have *s* constants that approach or equal those for the most dipolar conventional phases, and which are very much larger than those for the unsubstituted poly(methylphenylsiloxane) phases (C–H). The *SSP* parameter (see Table I) is very nearly the same, however, for phase H as for phases T–W.

All the phases in Tables I and III, other than squalane (A), are hydrogen-bond bases and so give rise to significant values of the *a* constant. Of the conventional phases K, L, O, P and Q are the most basic, and hence will preferentially interact with solutes that are hydrogen-bond acids. However, all the ionic salts except phase V are significantly stronger hydrogen-bond bases than any of the conventional phases. This is clearly due to the negatively charged counter anions. It is not coincidental that where charge dispersion in the anion is very large, as with phase V, the *a* constant decreases considerably.

The *l* constant, on its own, is equivalent to $\Delta G_s^0(\mathrm{CH_2})$ in that both quantities describe the ability of a phase to separate adjacent members of a homologous series. For the 24 phases, we find that

$$\Delta G_s^0(\mathrm{CH_2}) = -44.9 - 816\,l \qquad (3)$$

with S.D. = 17 cal mol^{-1}, R = 0.9739 and No. = 24. Thus our general solvation equation, eqn. 1 or 2, includes, via the *l* constant, all the information contained in $\Delta G_s^0(\mathrm{CH_2})$.

If the dependent variable, log*SP*, in eqn. 1 is based on retention times, then the characteristic constants *r*, *s*, *a*, *b* and *l* will be the same as if log*K* had been used as the dependent variable. Only the *c* constant changes. For many purposes, the *c* constant is not needed in the set of characteristic constants, but if log*K* is used as the dependent variable, combination of the *c* constant and the *l* constant can lead to extra information.

Suppose we consider only the rare gases and the alkanes, for which $R_2 = \pi_2^H = \alpha_2^H = \beta_2^H = 0$, so that eqn. 2 then becomes

$$\log K\,(\text{inert solute}) = c + l \log L^{16} \qquad (4)$$

The value of c is now identical with log K for an inert solute with $\log L^{16} = 0$, *i.e.*, a rare gas between krypton (−0.211) and xenon (0.378) or an alkane between methane (−0.323) and ethane (0.492). We can now combine the c constant and the l constant, via eqn. 4, to show exactly how the affinity of a stationary phase for an inert solute depends on the L^{16} value of the solute. In Fig. 1 is a plot of log K calculated through eqn. 4 against log L^{16} for a series of *n*-alkanes on phases R, T and Q. For any alkane, phase R always has the highest log K value, *i.e.*, the highest affinity, of the three phases. However, for phases T and Q there is a "cross-over" point between propane and *n*-butane, so that for small alkanes phase Q has more affinity, but for larger alkanes phase T has the greater affinity.

The l constant, as with $\Delta G_s^0(CH_2)$, gives only the slopes of the lines in Fig. 1. Combination of the l constant with the c constant leads to extra information on the affinity of the stationary phase for inert solutes.

We can quantify the interaction of solutes with stationary phases by calculating each term in eqn. 1 or, for the present purpose, each term in eqn. 2. The results are given in Table IV, using three particular solutes suggested by Poole and co-workers [7] as test probes. *n*-Butylbenzene was used as a test probe for dispersive interactions, octan-1-ol for solvent basicity, benzodioxane for solvent acidity (not relevant here) and nitrobenzene for "orientation interactions". However, examination of Table IV shows, as mentioned in the Introduction, that it is not possible to define a set of test probes in which each probe corresponds to a unique interaction. Thus, octan-1-ol, the test probe for solvent basicity (the α_2^H term), actually interacts with most solvents more through dipolar interactions (the $s\pi_2^H$ term) than through solute hydrogen-bond acid–solvent hydrogen-bond base interactions. It is useful to break down the $l \log L^{16}$ term into an exoergic dispersion contribution to the Gibbs energy of solution, leading to a positive contribution to log K, and an endoergic cavity contribution to the Gibbs energy of solution, leading to a negative contribution to log K. Abraham and Fuchs [15] dissected log L^{16} values into various contributions and if we calculate these for the test solutes in hexadecane, and assume that the proportions are relatively the same in the phases studied here, we obtain the results in the last two columns of Table IV. Now, even if these dispersive and cavity interactions are only very approximate, they do show, as we have suggested before [10], that the main exoergic contribution to solution of gaseous solutes in nearly all liquid phases (except water perhaps) is through solute–solvent dispersion interactions. Unfortunately, it is very difficult to devise a simple experimental solute parameter that will reflect only the ability of a solute to interact via dispersion forces. Hence our combined dispersion plus cavity term, logL^{16}, has to be used in the general solvation equation, and then broken down approximately into its constituents.

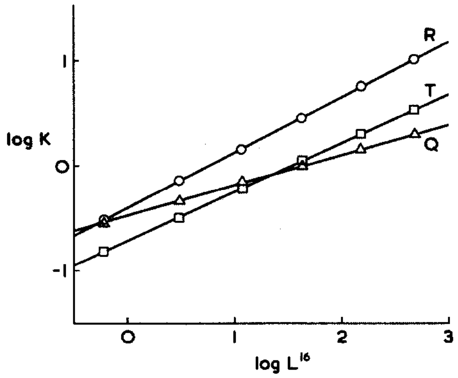

Fig. 1. Plot of log K against log L^{16} for the *n*-alkanes methane to hexane on phases R, T and Q.

Finally, we consider a few individual phases, and then show how the characteristic constants can be used to select phases for particular separations. Phases A–J are not exceptional; their dipolarities and hydrogen-bond basicities gradually increase along the series. Phase K has a very high dipolarity and basicity but the very low value of the l constant would tend to reduce the general usefulness of the phase. Phase M is exceptional, in that it has a moderate dipolarity ($s = 1.101$) but has effectively zero basicity, a most unusual occurrence. Of the molten salts, the tributylammonium salt, phase T, is of interest in that the Bu_3NH^+ group would be expected to be a powerful hydrogen-bond acid, but for this phase, as with all others, we find that the b constant is zero. No doubt intramolecular hydrogen bonding

TABLE IV

TERM-BY-TERM QUANTITATIVE EVALUATION OF THE SOLUTE–STATIONARY PHASE INTERACTIONS THAT CONTRIBUTE TO log K IN EQN. 2

Solute	Phase	c	rR_2	$s\pi_2^H$	$a\alpha_2^H$	$l \log L^{16}$	Dispersion[a]	Cavity[a]
Butylbenzene	C	−0.18	0.02	0.17	0	2.36	4.63	−2.27
	K	−0.64	0.23	0.99	0	1.13	2.22	−1.09
	M	−0.25	−0.22	0.57	0	1.95	3.83	−1.88
	Q	−0.49	0.17	0.99	0	1.36	2.67	−1.31
	R	−0.40	0.14	0.43	0	2.47	4.85	−2.38
	T	−0.72	0.07	0.80	0	2.18	4.28	−2.10
Octan-1-ol	C	−0.18	0.01	0.14	0.06	2.32	4.79	−2.47
	K	−0.64	0.08	0.80	0.61	1.11	2.29	−1.18
	M	−0.25	−0.07	0.46	0.02	1.92	3.96	−2.04
	Q	−0.49	0.06	0.80	0.62	1.34	2.77	−1.43
	R	−0.40	0.05	0.35	0.12	2.43	5.02	−2.59
	T	−0.72	0.02	0.65	1.08	2.15	4.44	−2.29
Nitrobenzene	C	−0.18	0.03	0.36	0	2.27	4.16	−1.89
	K	−0.64	0.34	2.09	0	1.09	2.00	−0.91
	M	−0.25	−0.32	1.21	0	1.88	3.45	−1.57
	Q	−0.49	0.24	2.10	0	1.31	2.40	−1.09
	R	−0.40	0.20	0.91	0	2.38	4.36	−1.98
	T	−0.72	0.10	1.70	0	2.10	3.85	−1.75

[a] These represent a breakdown of the $l \log L^{16}$ term according to ref. 15.

between the Bu_3NH^+ group and the counter anion takes place, so that the potential for intermolecular hydrogen bonding is reduced to zero. A comparison of the phases S, T and U shows that the a constant is reduced in phase T even though all three phases contain the 4-toluenesulphonate anion. This would be the result if there were intramolecular hydrogen bonding in phase T, because the anion would not then be totally available for intermolecular hydrogen bonding to a solute that was a hydrogen-bond acid.

For the separation of non-polar solutes, the only relevant characteristic constant is l. Phases A–F and R all have $l \geqslant 0.50$ and will be the best phases in the set to use. In order to separate compounds that are dipolar and non-acidic, a phase with a large s constant (and preferably a large l constant) is required. Phases J, L, M and O and the molten salts T, U, V and W are preferred here. These phases, except M, will also selectively absorb hydrogen-bond acids because they all have large a constants. To absorb acids rather than simply dipolar compounds requires $a \gg s$, if possible, and here the molten salts seem to be preferred (see Table IV).

In conclusion, we show that our general solvation equation, eqn. 1 or 2, can be used to analyse GLC retention data, both to classify stationary phases and to select phases for particular separations. The method is quantitative in that specific solute–stationary phase interactions can be identified and their contribution to the overall retention process can be evaluated (Table IV).

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