

Hydrogen bonding

XXVIII. Comparison of the solvation theories of Abraham and Poole, using a new acidic gas–liquid chromatography stationary phase

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ABSTRACT

The solvation theories of Abraham and of Poole have been applied to gas–liquid partition coefficients, $\log K$, for 62 varied solutes on bis(3-allyl-4-hydroxyphenyl)sulphone, with all K values corrected for interfacial adsorption. Application of the general solvation equation of Abraham, $\log K = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l \log L^{16}$, to $\log K$ values at 121 and 176°C shows that the new phase has considerable hydrogen-bond acidity.

The solvation equation of Poole, $\Delta G_s^{\text{SOLN}}(X) = \Delta G_s^{\text{CAV+DISP}}(X) + \Delta G_s^{\text{INT}}(X)$, was also applied to $\log K$ values at 121°C. It was shown that the terms $(rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H)$ and $-\Delta G_s^{\text{INT}}(X)/RT$ agreed to within 0.12 log unit for the total interaction effect for 23 varied solutes. Likewise, the combined cavity plus dispersion terms $(c + l \log L^{16})$ and $-\Delta G_s^{\text{CAV+DISP}}(X)/RT$ agreed to within 0.11 log unit for the same 23 solutes.

It is concluded that the solvation theories of Abraham and of Poole are entirely compatible and, indeed, yield essentially the same qualitative and quantitative results.

INTRODUCTION

Two of the most widely used solvation models in gas–liquid chromatography (GLC) are those of Abraham and co-workers and of Poole and co-workers. Since these have been described in detail [1,2] we give only a summary of these

models. Both are derived from a cavity model of solvation [3–5], in which the process of solvation of a gaseous solute is broken down into three stages: (1) A cavity of suitable size to accommodate the solute must be created in the solvent; work is required in order to disrupt solvent–solvent interactions and hence this process is endoergic. (2) Solvent molecules round the cavity are reorganised; the Gibbs energy change for

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this process is generally assumed to be negligible [4], but we note that this is not the case in terms of enthalpy or entropy. (3) The solute is introduced into the cavity, and various solute–solvent interactions are set up, all of which are exoergic. The dissolution of a gaseous solute into a solvent or GLC stationary phase, as measured by K (or L), the gas–liquid partition coefficient (eqn. 1), will therefore depend on the balance between the endoergic stage (1) opposing solution and the exoergic stage (3) that aids solution. In both the Abraham and the Poole models, the system for analysis consists of a set of retention data, preferably as $\log K$ values, for a series of solutes on a given stationary phase. Hence the solvent properties remain constant, and a major task is to define suitable solute properties or descriptors, through which some understanding of the solvation process can be obtained.

$$K \text{ (or } L) = \frac{\text{concentration of solute in solution}}{\text{concentration of solute in the gas phase}} \quad (1)$$

Abraham and co-workers [5–10] attempted to find descriptors that would reflect the ability of a solute to take part in the various solute–solvent interactions that could be set up in stage (3) above. The general solvation equation of Abraham contains the solute descriptors R_2 (an excess molar refraction [6] that reflects some general dispersion interactions), π_2^H (a dipolarity/polarisability parameter [7]), and α_2^H and β_2^H (the solute hydrogen-bond acidity and hydrogen-bond basicity respectively [7,8]). It should be noted that α_2^H and β_2^H are the effective or summation acidity and basicity ($\Sigma \alpha_2^H$ and $\Sigma \beta_2^H$) appropriate for the situation in which a solute is surrounded by an excess of solvent molecules [10]. The final solute descriptor is $\log L^{16}$, where L^{16} is the gas–liquid partition coefficient on hexadecane at 25°C [9], and includes the important cavity term plus a general dispersion interaction term. All these descriptors are included in eqn. 2, where the coefficients c , r , s , a , b and l are found by the method of multiple linear regression analysis and serve as constants that characterise the solvent or stationary phase under investigation.

$$\log K = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l \log L^{16} \quad (2)$$

In the approach of Poole and co-workers [2,11] the standard Gibbs energy change for solvation of a solute X , in a solvent s ,

$$\Delta G_s^{\text{SOLN}}(X) = -RT \ln K(X) \quad (3)$$

is considered to be made up of a cavity term, a non-polar term and a polar term,

$$\Delta G_s^{\text{SOLN}}(X) = \Delta G_s^{\text{CAV}}(X) + \Delta G_s^{\text{NP}} + \Delta G_s^{\text{P}} \quad (4)$$

Once again, it is not possible to obtain the cavity term, $\Delta G_s^{\text{CAV}}(X)$ separately, and so Poole et al. [2] deconvoluted $\Delta G_s^{\text{SOLN}}(X)$ into an experimentally more accessible form,

$$\Delta G_s^{\text{SOLN}}(X) = \Delta G_s^{\text{SOLN}}(\text{HC})^V + \Delta G_{\text{SQ}}^{\text{P}}(X) + \Delta G_s^{\text{INT}}(X) \quad (5)$$

where $\Delta G_s^{\text{SOLN}}(\text{HC})^V$ is the Gibbs energy change for solvation of a hydrocarbon, of the same Van der Waals volume as X , into solvent s , and $\Delta G_{\text{SQ}}^{\text{P}}(X)$ is the polar contribution to solvation of solute X in squalane. The latter is experimentally obtained through

$$\Delta G_{\text{SQ}}^{\text{P}}(X) = \Delta G_{\text{SQ}}^{\text{SOLN}}(X) - \Delta G_{\text{SQ}}^{\text{SOLN}}(\text{HC})^V \quad (6)$$

and so only the term $\Delta G_s^{\text{INT}}(X)$ in eqn. 5 is unknown, and hence can be obtained by difference [11]. In eqn. 5, the sum of $\Delta G_s^{\text{SOLN}}(\text{HC})^V$ and $\Delta G_{\text{SQ}}^{\text{P}}(X)$ represents the cavity term plus a general dispersion interaction term and so can be represented as

$$\Delta G_s^{\text{SOLN}}(X) = \Delta G_s^{\text{CAV+DISP}}(X) + \Delta G_s^{\text{INT}}(X) \quad (7)$$

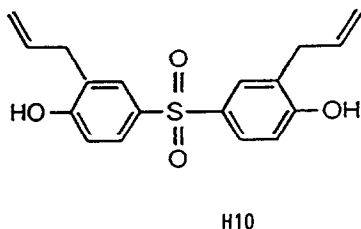
A simple rearrangement of the general solvation equation, eqn. 2, shows clearly the connection between eqns. 2 and 7,

$$\log K = (c + l \log L^{16}) + (rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H) \quad (8)$$

The cavity plus dispersion term of eqn. 7 is equivalent to the constant plus the $l \log L^{16}$ term of eqn. 2, and the interaction term of eqn. 7 is equivalent to the sum of all the individual interaction terms in eqn. 2.

Kollie *et al.* [1] used the carefully obtained log K values of Kollie and Poole [11,12] to test these supposed equivalences. They showed that for 30 various solutes on 25 stationary phases there was excellent agreement between $(c + l \log L^{16})$ [13] and log K (CAV + DISP), the latter being used instead of the Gibbs energy term in eqn. 7. For the same sets of solutes and phases, there was again excellent agreement between the two interaction terms $(rR_2 + s\pi_2^H + a\alpha_2^H)$ [13] and log K (INT). In this analysis of Poole and Abraham, the interaction term of eqn. 8 was reduced to the term $(rR_2 + s\pi_2^H + a\alpha_2^H)$ because none of phases studied was a significant hydrogen-bond acid: hence the solute hydrogen-bond basicity was unnecessary.

It seemed important to compare the two equations of Abraham and Poole for the more general case when all the interaction terms in eqn. 8 are significant. Although all the commercially available GLC stationary phases are either non-acidic or only poorly acidic, Abraham *et al.* [14] showed in a preliminary survey that bis(3-allyl-4-hydroxyphenyl)sulphone, which we denote as H10, had significant hydrogen-bond acidity at 175°C, *i.e.* some 30°C above its melting point. We have therefore prepared a further quantity of H10 in order to investigate its chromatographic properties more thoroughly, and in order to compare the methods of Abraham and Poole with a stationary phase that has considerable hydrogen-bond acidity.



EXPERIMENTAL

The stationary phase H10 was prepared exactly as described before [14]. Its density was determined using a micro Lapkin bicapillary pycnometer over the range 145–180°C, and the density values fitted to the equation

$$\rho(\text{H10}) = 1.3602 - 0.001119 T (\text{°C}) \quad (9)$$

Column packings containing from 8 to 20% (w/w) of H10 on Chromosorb W AW (60–80 mesh, 0.18–0.25 mm) were prepared using the rotary evaporator technique. The damp packing was dried in a fluidized bed drier and packed into 2.0 m × 2 mm glass columns with the aid of suction and gentle vibration. Columns were conditioned at the temperature used in the investigation until a stable baseline and invariant retention times and symmetrical peaks for a test mixture of compounds was obtained. Accurate phase loadings were determined by Soxhlet extraction for 72 h of an aliquot of the used packing with the same solvent selected for coating. For column evaluation a 3700 gas chromatograph (Varian Instruments, Palo Alto, CA, USA) with heated on-column injectors and a flame ionization detector was used. Column temperatures were measured with a NIST-certified (National Institute of Standards, USA) mercury thermometer to $\pm 0.2^\circ\text{C}$ and averaged over the column cavity. The column pressure drop was measured with a mercury manometer to ± 1 mmHg (1 mm Hg = 133.322 Pa). The carrier gas was helium, adjusted to a known flow-rate of about 20 ml/min using a thermostated soap-film bubble meter. Samples of 1–10 μl of headspace vapours were injected onto the column by a gas-tight syringe. Several injections at different amounts were made to ensure that the conditions for infinite dilution/zero surface coverage were met.

The gas–liquid partition coefficients were calculated [15–17] by linear extrapolation to infinite phase volume of plots of the net retention volume per gram of column packing/volume of liquid phase against the reciprocal of the volume of liquid phase. A minimum of four column packings was used to span the phase loading of 8–20% (w/w) in reasonably equal increments. This procedure was carried out in order to correct the observed net retention volumes for any contribution due to interfacial adsorption.

Retention data were obtained at 176.2°C and at 121.2°C, where H10 at the latter temperature exists as a supercooled liquid. The corrected gas→liquid partition coefficients are listed in Table I together with corresponding standard deviations (S.D.).

TABLE I
VALUES OF *K* AND log *K* ON PHASE H 10 AT 176°C AND 121°C

Solute	<i>K</i> (176)	S.D.	log <i>K</i> (176)	<i>K</i> (121)	S.D.	log <i>K</i> (121)
Dodecane	13.68	0.87	1.136	52.88	0.44	1.723
Tridecane	24.95	3.70	1.397	97.35	0.66	1.988
Tetradecane	34.54	7.00	1.538	176.28	1.43	2.246
Pentadecane	55.83	4.70	1.747	291.06	3.05	2.464
Hexadecane	82.65	10.90	1.917	506.82	1.07	2.705
cis-Hydrindane	24.92	1.60	1.397	45.44	0.95	1.657
Oct-2-yne				34.37	0.96	1.536
Dodec-1-yne	34.16	4.60	1.534	259.96	0.96	2.415
1,1,2,2-Tetrachloroethane	46.47	3.62	1.667	223.91	1.03	2.350
Di-n-hexylether	93.58	1.06	1.971	709.76	0.97	2.851
1,2-Diethoxyethane	212.00	41.60	2.326	6526.14	0.98	3.815
1,4-Dioxane	54.54	0.19	1.737	228.22	0.95	2.358
Nonanal	145.58	0.21	2.163	866.23	0.96	2.938
Pentan-2-one	39.04	1.25	1.592	167.33	0.95	2.224
Hexan-2-one	52.22	3.61	1.718	196.46	0.98	2.293
Heptan-2-one	84.56	2.58	1.927	476.98	0.97	2.679
Octan-2-one	123.01	6.93	2.090	716.68	0.99	2.855
Nonan-2-one				1231.95	2.25	3.091
Methyl heptanoate	71.39	5.23	1.854	462.65	0.98	2.665
Methyl octanoate	109.17	8.66	2.038	679.00	1.00	2.832
Methyl nonanoate	160.28	9.70	2.205	1152.93	1.03	3.062
Methyl decanoate	224.25	17.60	2.351	2208.02	1.01	3.344
Methyl undecanoate	323.11	27.85	2.509	3273.47	1.11	3.515
1-Nitropropane	42.85	2.49	1.632	215.21	0.96	2.333
1-Nitropentane	92.04	1.87	1.964	572.69	0.95	2.758
1-Nitrohexane	143.40	0.74	2.157	924.91	0.98	2.966
Nitrocyclohexane				1575.14	1.01	3.197
Dimethylformamide	1032.00	24.60	3.014	3739.66	0.97	3.573
Dimethylacetamide	2601.00	13.50	3.415			
Butan-1-ol	38.34	3.25	1.584	199.85	0.96	2.301
Pentan-1-ol	73.55	1.16	1.867	352.21	0.97	2.547
Hexan-1-ol	111.07	0.29	2.046	617.07	0.96	2.790
2-Methylpentan-2-ol	39.61	1.07	1.598	199.85	0.96	2.301
Heptan-1-ol	164.75	1.83	2.217	1077.74	1.07	3.033
Octan-1-ol	237.51	0.97	2.376	1488.48	0.96	3.173
Nonan-1-ol	346.87	4.73	2.540	1806.63	0.96	3.257
Dimethylsulphoxide	6009.60	16.80	3.779			
Benzene	7.96	0.10	0.901	27.81	0.96	1.444
Toluene	15.36	0.38	1.186	45.15	0.96	1.655
Ethylbenzene	24.54	0.86	1.390	79.72	0.95	1.902
Butyl benzene	41.23	4.30	1.615	137.86	0.97	2.139
Chlorobenzene	33.81	1.92	1.529	95.38	0.95	1.979
<i>o</i> -Dichlorobenzene	109.13	1.55	2.038	251.97	0.23	2.401
Bromobenzene	67.93	0.64	1.832	159.78	0.95	2.204
Iodobenzene	131.86	0.12	2.120	373.89	0.95	2.573
Anisole	64.89	3.06	1.812	253.01	0.96	2.403
Benzaldehyde	260.14	1.21	2.415	1012.55	0.98	3.005
Acetophenone	531.76	0.29	2.726	2410.16	1.03	3.382
Benzonitrile	312.03	0.75	2.494	1207.82	0.97	3.082
2,6-Dimethylaniline	549.20	2.61	2.740	3483.72	1.21	3.542

TABLE I (Continued)

Solute	K(176)	S.D.	log K(176)	K(121)	S.D.	log K(121)
N-Methylaniline	304.34	0.53	2.483	1997.25	1.01	3.300
N,N-Dimethylaniline	191.29	1.65	2.282	1119.13	1.00	3.049
Nitrobenzene	395.38	0.93	2.597	1713.06	0.97	3.234
Phenol	289.30	0.68	2.461	1756.01	0.98	3.245
<i>m</i> -Cresol	426.70	1.51	2.630			
<i>p</i> -Cresol	429.90	0.01	2.633	2783.37	1.04	3.445
2,5-Dimethylphenol				4634.74	0.97	3.666
2,6-Dimethylphenol				2913.68	0.97	3.464
3,5-Dimethylphenol				4908.81	1.05	3.691
4-Chlorophenol	945.80	2.19	2.976	7802.55	1.02	3.892
1,4-Benzodioxane				2225.62	0.96	3.347
Pyridine	181.68	15.80	2.259	352.66	0.94	2.547

RESULTS AND DISCUSSION

The useful liquid range for the stationary phase H10 is 150–220°C, but it can also be used in the supercooled state from 150°C down to around 100°C. There is some loss in efficiency at these lower temperatures due to the high viscosity of the material, but it is very useful to obtain retention data at 121°C in order to compare present results with those previously obtained at 121.4°C [11,12]. We found that contributions from interfacial adsorption were considerable, especially at 121°C rather than 176°C, and especially with alkanes as solutes. Some examples of the contribution of gas–liquid partition and interfacial adsorption to the obtained specific retention volumes, V_G , are given in Table II. The large contribution of interfacial adsorption in the case of alkanes on the polar phase H10 reinforces the previous warning of Poole and co-workers [18,19] of the deficiencies of the McReynolds system, which relies on retention data for alkanes. On the other hand, the approach of Poole is not tied to alkane data on polar phases at all, and in the method of Ab-

raham, data on alkanes are not essential—all that is required for the application of eqn. 2 is a set of retention data for any wide range of solutes.

Characterisation of H10 by the method of Abraham is straightforward. The necessary solute descriptors [6–10,13] are in Table III, and application of the general solvation equation, eqn. 2 yields an excellent equation for log K at 121.2°C. In eqn. 10 and elsewhere, n is the number of solutes, r is the overall correlation coefficient, S.D. is the regression standard deviation, and F is the Fisher F -statistic. The standard deviation of each coefficient is given below the coefficient. There are no outliers in eqn. 10, and for the one solute missing, that is 1,2-diethoxyethane, we lack the required descriptors. Eqn. 10 confirms that H10 is, indeed, a reasonably strong hydrogen-bond acid, with a b constant of 1.457 units at 121°C. It is also quite dipolar, with the s constant at 1.323 units near that for OV-225 or Carbowax 20M [13], and quite basic with the a constant at 1.266 units larger [13] than that for OV-225 (0.964) and nearly as large as that for tetrabutylammonium picrate (1.424).

$$\log K(121.2^\circ\text{C}) = -0.568 - 0.051R_2 + 1.323\pi_2^H + 1.266\alpha_2^H + 1.457\beta_2^H + 0.418 \log L^{16}$$

$$\begin{array}{cccccc} 0.060 & 0.044 & 0.052 & 0.052 & 0.070 & 0.010 \end{array}$$

$$n = 58, r = 0.9940, \text{S.D.} = 0.069, F = 856$$

(10)

TABLE II

EXAMPLES OF CONTRIBUTIONS FROM GAS-LIQUID PARTITION AND INTERFACIAL ADSORPTION TO V_G VALUES FOR SOLUTES ON H10 AT 121°C

V_G values in $\text{cm}^3 \text{g}^{-1}$. Phase loading 8.9% (w/w) H10.

Solute	V_G (exp)	V_G (partition)	V_G (adsorption)	% (adsorption) ^a
<i>n</i> -Dodecane	64.59	29.91	34.68	53.7
<i>n</i> -Tridecane	112.01	55.06	56.95	50.8
<i>n</i> -Tetradecane	194.72	99.71	95.01	48.8
<i>n</i> -Pentadecane	330.46	164.63	165.83	50.2
<i>n</i> -Hexadecane	567.17	286.67	280.50	49.5
<i>cis</i> -Hydrindane	27.79	25.70	2.09	7.5
Oct-2-yne	27.25	19.44	7.81	28.7
Heptan-2-one	312.59	269.79	42.80	13.7
Methyl nonanoate	828.23	652.13	176.10	21.3
1-Nitropentane	333.49	323.93	9.56	2.9
N,N-Dimethylformamide	2159.34	2115.25	44.09	2.0
Heptan-1-ol	746.64	609.60	137.04	18.4
Toluene	31.66	25.54	6.12	19.3
Anisole	161.55	143.11	18.44	11.4
Bromobenzene	94.49	90.37	4.12	4.4
Acetophenone	1528.49	1363.25	165.24	10.8
Phenol	1059.18	993.24	65.94	6.2
4-Chlorophenol	4585.81	4413.33	172.48	3.8

^a This is the % contribution of adsorption to V_G (exp) with a phase loading of 8.9%. The V_G (partition) values used to obtain the log K values, are those extrapolated as described in the text to zero contribution from adsorption.

TABLE III

DESCRIPTORS USED IN EQN. 2

Solute	R_2	π_2^H	α_2^H	β_2^H	$\log L^{16}$
Dodecane	0.000	0.00	0.00	0.00	5.696
Tridecane	0.000	0.00	0.00	0.00	6.200
Tetradecane	0.000	0.00	0.00	0.00	6.705
Pentadecane	0.000	0.00	0.00	0.00	7.209
Hexadecane	0.000	0.00	0.00	0.00	7.714
<i>cis</i> -Hydrindane	0.439	0.25	0.00	0.00	4.635
Oct-2-yne	0.225	0.30	0.00	0.10	3.850
Dodec-1-yne	0.133	0.23	0.13	0.10	5.657
1,1,2,2-Tetrachloroethane	0.595	0.76	0.16	0.12	3.803
Di- <i>n</i> -hexylether	0.000	0.25	0.00	0.45	5.938
1,2-Diethoxyethane	0.008		0.00		
1,4-Dioxane	0.329	0.75	0.00	0.64	2.892
Nonanal	0.150	0.65	0.00	0.45	4.856
Pentan-2-one	0.143	0.68	0.00	0.51	2.755
Hexan-2-one	0.136	0.68	0.00	0.51	3.262
Heptan-2-one	0.123	0.68	0.00	0.51	3.760
Octan-2-one	0.108	0.68	0.00	0.51	4.257

TABLE III (Continued)

Solute	R_2	π_2^H	α_2^H	β_2^H	$\log L^{16}$
Nonan-2-one	0.119	0.68	0.00	0.51	4.735
Methyl heptanoate	0.079	0.60	0.00	0.45	4.356
Methyl octanoate	0.065	0.60	0.00	0.45	4.838
Methyl nonanoate	0.056	0.60	0.00	0.45	5.321
Methyl decanoate	0.053	0.60	0.00	0.45	5.803
Methyl undecanoate	0.050	0.60	0.00	0.45	6.285
1-Nitropropane	0.242	0.95	0.00	0.31	2.894
1-Nitropentane	0.212	0.95	0.00	0.29	3.938
1-Nitrohexane	0.203	0.95	0.00	0.29	4.416
Nitrocyclohexane	0.441	0.97	0.00	0.31	4.826
N,N-Dimethylformamide	0.367	1.31	0.00	0.74	3.173
N,N-Dimethylacetamide	0.363	1.33	0.00	0.78	3.717
Butan-1-ol	0.224	0.42	0.37	0.48	2.601
Pentan-1-ol	0.219	0.42	0.37	0.48	3.106
Hexan-1-ol	0.210	0.42	0.37	0.48	3.610
2-Methylpentan-2-ol	0.169	0.30	0.31	0.60	3.081
Heptan-1-ol	0.211	0.42	0.37	0.48	4.115
Octan-1-ol	0.199	0.42	0.37	0.48	4.619
Nonan-1-ol	0.193	0.42	0.37	0.48	5.124
Dimethylsulphoxide	0.522	1.74	0.00	0.89	3.459
Benzene	0.610	0.52	0.00	0.14	2.786
Toluene	0.601	0.52	0.00	0.14	3.325
Ethylbenzene	0.613	0.51	0.00	0.15	3.778
<i>n</i> -Butylbenzene	0.600	0.51	0.00	0.15	4.730
Chlorobenzene	0.718	0.65	0.00	0.07	3.657
<i>o</i> -Dichlorobenzene	0.872	0.78	0.00	0.04	4.518
Bromobenzene	0.882	0.73	0.00	0.09	4.041
Iodobenzene	1.188	0.82	0.00	0.12	4.502
Anisole	0.708	0.75	0.00	0.29	3.890
Benzaldehyde	0.820	1.00	0.00	0.39	4.008
Acetophenone	0.818	1.01	0.00	0.48	4.501
Benzonitrile	0.742	1.11	0.00	0.33	4.039
2,6-Dimethylaniline	0.972	0.89	0.20	0.46	5.028
<i>N</i> -Methylaniline	0.948	0.90	0.17	0.45	4.478
<i>N,N</i> -Dimethylaniline	0.957	0.84	0.00	0.41	4.701
Nitrobenzene	0.871	1.11	0.00	0.28	4.557
Phenol	0.805	0.89	0.60	0.30	3.766
<i>m</i> -Cresol	0.822	0.88	0.57	0.34	4.310
<i>p</i> -Cresol	0.820	0.87	0.57	0.31	4.312
2,5-Dimethylphenol	0.840	0.79	0.54	0.37	4.774
2,6-Dimethylphenol	0.860	0.79	0.39	0.39	4.680
3,5-Dimethylphenol	0.820	0.84	0.57	0.36	4.856
4-Chlorophenol	0.915	1.08	0.67	0.20	4.775
1,4-Benzodioxan	0.874	1.07	0.00	0.35	4.971
Pyridine	0.631	0.84	0.00	0.52	3.022

The corresponding equation for $\log K$ (176.2°C) is disappointing, with a correlation

$$\log K(176.2^\circ\text{C}) = -0.749 + 0.165R_2 + 1.160\pi_2^H + 0.808\alpha_2^H + 1.290\beta_2^H + 0.332\log L^{16}$$

$$\begin{matrix} 0.123 & 0.088 & 0.096 & 0.105 & 0.139 & 0.020 \end{matrix}$$

$$n = 54, r = 0.9738, \text{S.D.} = 0.134, F = 176$$

(11)

coefficient lower than usual, and a standard deviation higher than usual, in this type of work. The rather poor equation can hardly be due to poorly-determined descriptors, because eqn. 10 is quite reasonable. Neither are there any obvious outliers —dimethylacetamide (but not dimethylformamide) is out by just over two standard deviations, but removal of this solute has little effect, with F increasing from 176.2 to only 178.5. However, the trend in the main constants, s , a , b and l is as expected. All of these are lower at 176.2°C than at 121.2°C.

It is of considerable interest to compare the acidic phase H10 with a phase recently studied at 80°C by Li *et al.* [20] 4-dodecyl- α , α -bis(trifluoromethyl)benzyl alcohol, which we denote as BOH. Li *et al.* [20] did not actually characterise BOH, because their intention was to use this phase to obtain solute hydrogen-bond basicities. However, we have [6–10] all the necessary descriptors for 143 out of 146 solutes studied by Li *et al.* [20] leading to the regression equation (eqn. 12), where K' is a relative partition coefficient.

Although eqn. 12 is very poor, it does show that BOH has zero hydrogen-bond basicity, but is a very strong hydrogen-bond acid. Even though eqn. 12 refers to 80°C, rather than to 121°C as does eqn. 11, it is likely that BOH is a considerably stronger hydrogen-bond acidic phase than is H10. Unfortunately, the poor quality of eqn. 12 precludes the use of BOH, at 80°C, to determine further values of β_2^H since the projected error in any back-calculated β_2^H value is too large (estimated as S.D./ $b = 0.099$).

We thought it useful also to characterise the corresponding ether of Li *et al.* [20], BOMe, and

if carboxylic acids and n -hexylamine are excluded we obtain eqn. 13. As found by Li *et al.* [20] using either 59 or 87 solutes, BOMe is slightly polar, non-basic, but is a weak hydrogen-bond acid, again at 80°C.

The method of Poole starts with the total standard Gibbs energy of solvation, $\Delta G^{\text{SOLN}}(\text{X})$, which at 121.2°C can be transformed into a $\log K(\text{T})$ term through the factor $\Delta G^{\text{SOLN}} = -1.804 \log K(\text{T})$, where the parenthesised T denotes the total solvation energy term. The $\Delta G^{\text{INT}}(\text{X})$ term and the $\Delta G^{\text{CAV+DISP}}(\text{X})$ term can similarly be transformed into a $\log K(\text{INT})$ and a $\log K(\text{C} + \text{D})$ term, and are given in Table IV for the set of test solutes used previously by Kollie and Poole [11,12]. Depending on the solute, either the interaction term or the (cavity plus dispersion) term can be the larger. However, the latter composite term will include a rather large cavity term that would result in positive values of ΔG_s^O , and hence in negative values of $\log K(\text{C} + \text{D})$, together with a dispersion term that favours solution and would lead to positive $\log K(\text{C} + \text{D})$ values. Clearly the dispersion term always outweighs the cavity effect, and probably is the most important single solute-solvent interaction. The $\log K(\text{INT})$ values for the alcohols are amongst the largest interaction terms, and show clearly the effect of the acidic and basic stationary phase on these amphoteric compounds.

The analysis of Abraham can be used to breakdown the total interaction term ($rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H$) into component parts, as shown also in Table IV. The dipolar and polarisable aromatic compounds such as benzonitrile and nitrobenzene give rise to large $s\pi_2^H$ terms, the phenols (as expected) show the largest $a\alpha_2^H$

$$\log K'(\text{BOH}) = -1.598 - 0.223R_2 + 0.447\pi_2^H + 2.686\beta_2^H + 0.678 \log L^{16}$$

0.095	0.121	0.119	0.125	0.026
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$$n = 143, r = 0.9598, \text{S.D.} = 0.265, F = 402.9 \quad (12)$$

$$\log K'(\text{BOMe}) = -1.440 + 0.411\pi_2^H + 0.166\beta_2^H + 0.691 \log L^{16}$$

0.018	0.016	0.024	0.005
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$$n = 140, r = 0.9977, \text{S.D.} = 0.053, F = 9761.6 \quad (13)$$

TABLE IV
BREAKDOWN OF SOLUTE-SOLVENT EFFECTS ACCORDING TO THE METHODS OF ABRAHAM AND POOLE

Solute	Poole ^a		Abraham ^b		$\log K(T)$	$\log K(C+D)$	$\log K(NT)$	rR_2	$\sigma_{H_2}^H$	αa_2^H	$\beta \rho_2^H$	$f / \log L^{10}$	INT ^c	(C+D) ^c	T ^d
	$\log K(NT)$	$\log K(C+D)$	c	c											
cis-Hydrindane	0.275	1.382	-0.57	-0.02	1.657			0.33	0.00	0.00	0.00	1.94	0.33	1.35	1.68
Oct-2-yne	0.626	0.910	-0.57	-0.01	1.536			0.40	0.00	0.00	0.15	1.61	0.54	1.03	1.57
Dodec-1-yne	0.688	1.727	-0.57	-0.01	2.415			0.30	0.16	0.15	0.15	2.36	0.61	1.79	2.40
1,1,2,2-Tetrachloroethane	1.278	1.072	-0.57	-0.03	2.350			1.01	0.20	0.17	0.17	1.59	1.38	0.99	2.37
Di-n-hexylether	0.998	1.854	-0.57	0.00	2.852			0.33	0.00	0.66	0.66	2.48	0.99	1.91	2.90
1,4-Dioxane	1.888	0.471	-0.57	-0.02	2.359			0.99	0.00	0.93	1.21	1.92	1.92	0.62	2.55
Nonanal	1.537	1.401	-0.57	-0.01	2.938			0.86	0.00	0.66	0.66	2.03	1.52	1.45	2.97
Octan-2-one	1.722	1.134	-0.57	-0.01	2.856			0.90	0.00	0.74	1.78	1.78	1.64	1.21	2.85
1-Nitropropane	1.849	0.484	-0.57	-0.01	2.333			1.26	0.00	0.45	0.45	1.21	1.71	0.63	2.34
1-Nitropentane	1.764	0.994	-0.57	-0.01	2.758			1.26	0.00	0.42	0.42	1.65	1.68	1.07	2.75
Butan-1-ol	2.072	0.229	-0.57	-0.01	2.301			0.56	0.47	0.70	0.70	1.09	1.72	0.51	2.23
2-Methylpentan-2-ol	1.823	0.478	-0.57	-0.01	2.301			0.40	0.39	0.87	0.87	1.29	1.66	0.71	2.37
Octan-1-ol	1.870	1.303	-0.57	-0.01	3.173			0.56	0.47	0.70	0.70	1.93	1.72	1.35	3.08
Benzene	0.954	0.490	-0.57	-0.03	1.444			0.69	0.00	0.20	0.20	1.16	0.89	0.57	1.46
n-Butylbenzene	0.688	1.452	-0.57	-0.03	2.140			0.67	0.00	0.22	0.22	1.98	0.89	1.38	2.27
Anisole	1.304	1.100	-0.57	-0.04	2.404			0.99	0.00	0.42	0.42	1.63	1.41	1.02	2.44
Benzonitrile	1.918	1.164	-0.57	-0.04	3.082			1.47	0.00	0.48	0.48	1.69	1.95	1.08	3.03
2,6-Dimethylaniline	1.828	1.714	-0.57	-0.05	3.542			1.18	0.25	0.67	0.67	2.10	2.10	1.48	3.58
N-Methylaniline	1.843	1.458	-0.57	-0.05	3.301			1.19	0.22	0.66	0.66	1.87	2.06	1.26	3.32
N,N-Dimethylaniline	1.496	1.553	-0.57	-0.05	3.049			1.11	0.00	0.60	0.60	1.97	1.71	1.35	3.06
Nitrobenzene	1.741	1.493	-0.57	-0.04	3.234			1.47	0.00	0.41	0.41	1.90	1.88	1.29	3.17
Phenol			-0.57	-0.04				1.47	0.76	0.44	0.44	1.57	2.37	0.97	3.34
4-Chlorophenol			-0.57	-0.05				1.43	0.85	0.29	0.29	2.00	2.57	1.38	3.95
1,4-Benzodioxan	1.654	1.694	-0.57	-0.04	3.348			1.42	0.00	0.51	0.51	2.08	1.93	1.47	3.39
Pyridine	1.913	0.635	-0.57	-0.03	2.548			1.11	0.00	0.76	0.76	1.26	1.87	0.66	2.53

^a According to eqn. 7, with $\log K$ instead of Gibbs energy.

^b According to eqn. 2.

^c Terms summed as shown in eqn. 8.

^d Total of the previous two columns.

terms, and compounds such as dioxane and the nitrogen bases give large $b\beta_2^H$ terms. In all cases however, the composite $l \log L^{16}$ term is larger than any given interaction term; since, again, the $l \log L^{16}$ term includes a general dispersion interaction favouring solution, and a cavity effect opposing solution, it may be deduced that the general dispersion interaction must be by far the largest individual interaction.

If the total interaction term ($rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H$) is summed and denoted INT, and the dispersion plus cavity effects ($c + l \log L^{16}$)^a are summed and denoted as (C + D), then it is possible to make a straight comparison between the results of Poole's analysis and those of the analysis of Abraham. In Table IV, the entries under $\log K(\text{INT})$ can be compared directly with those under the heading INT. There is very good agreement between the two sets of data, the average difference being only 0.12 log unit. Similarly, the average difference between the Poole term, $\log K(\text{C} + \text{D})$, and the Abraham term (C + D) is only 0.11 log units.

The approaches of Poole and Abraham are rather different. In the Poole system, the term $\Delta G_s^{\text{CAV} + \text{DISP}}$, corresponding to $\log K(\text{C} + \text{D})$ in Table IV, is obtained using retention data on squalane, and the ΔG_s^{INT} term, corresponding to $\log K(\text{INT})$ in Table IV, is obtained by difference through eqn. 7. In the Abraham system, a breakdown of observed $\log K$ values into various interactions is obtained through multiple linear regression analysis, using eqn. 2 and solute descriptors as outlined in the Introduction. However, when the various terms in eqn. 2 are summed so as to correspond to Poole's INT and (CAV + DISP) terms, there is excellent agreement between the two sets of data for 23 varied solutes on a phase, bis(3-allyl-4-hydroxyphenyl)-sulphone, that can interact through a number of

effects including two types of hydrogen-bonding (solute acid–solvent base, and solute base–solvent acid). Taken together with our previous results using 25 non-acidic stationary phases [1], our overall conclusion is that the solvation models of Abraham and Poole are entirely compatible, and when applied to experimental retention data, as outlined in this work, yield essentially the same qualitative and quantitative results.

REFERENCES

- 1 T.O. Kollie, C.F. Poole, M.H. Abraham and G.S. Whiting, *Anal. Chim. Acta*, 259 (1992) 1.
- 2 C.F. Poole, T.O. Kollie and S.K. Poole, *Chromatographia*, 34 (1992) 281.
- 3 R.A. Pierotti, *Chem. Revs.*, 76 (1976) 717.
- 4 M.H. Abraham and J. Liszi, *J. Chem. Soc., Faraday Trans. 1*, 74 (1978) 1604.
- 5 M.H. Abraham, P.L. Grellier, I. Hamerton, R.A. McGill, D.V. Prior and G.S. Whiting, *Faraday Disc. Chem. Soc.*, 85 (1988) 107.
- 6 M.H. Abraham, G.S. Whiting, R.M. Doherty and W.J. Shuely, *J. Chem. Soc., Perkin Trans. 2*, (1990) 1451.
- 7 M.H. Abraham, G.S. Whiting, R.M. Doherty and W.J. Shuely, *J. Chromatogr.*, 587 (1991) 213.
- 8 M.H. Abraham and G.S. Whiting, *J. Chromatogr.*, 594 (1992) 229.
- 9 M.H. Abraham, P.L. Grellier and R.A. McGill, *J. Chem. Soc., Perkin Trans. 2*, (1987) 797.
- 10 M.H. Abraham, *Chem. Soc. Rev.*, 22 (1993) 73.
- 11 T.O. Kollie and C.F. Poole, *J. Chromatogr.*, 556 (1991) 457.
- 12 T.O. Kollie and C.F. Poole, *J. Chromatogr.*, 550 (1991) 213.
- 13 M.H. Abraham, G.S. Whiting, R.M. Doherty and W.J. Shuely, *J. Chromatogr.*, 587 (1991) 229.
- 14 M.H. Abraham, I. Hamerton, J.B. Rose and J.W. Grate, *J. Chem. Soc., Perkin Trans. 2*, (1991) 1417.
- 15 B.R. Kersten, S.K. Poole and C.F. Poole, *J. Chromatogr.*, 468 (1989) 235.
- 16 S.K. Poole and C.F. Poole, *J. Chromatogr.*, 500 (1990) 329.
- 17 C.F. Poole, K.G. Furton, R.M. Pomaville, S.K. Poole and B.R. Kersten, *Molten Salt Techniques*, 4 (1990) 41.
- 18 B.R. Kersten, C.F. Poole and K.G. Furton, *J. Chromatogr.*, 411 (1987) 43.
- 19 S.K. Poole, B.R. Kersten and C.F. Poole, *J. Chromatogr.*, 471 (1989) 91.
- 20 J. Li, Y. Zhang, H. Ouyang and P.W. Carr, *J. Am. Chem. Soc.*, 114 (1992) 9813.

^a We include the constant c , in order to be able to compare these effects with the $\log K(\text{C} + \text{D})$ term of Poole. Note that in the Poole summation, there is no constant term at all.