Hydrogen bonding. Part 29.† Characterization of 14 Sorbent Coatings for Chemical Microsensors using a New Solvation Equation

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Gas–liquid partition coefficients, K, have been obtained for 20–70 solute analytes on 14 candidate phases for chemical microsensors at 298 K and on three of the phases at higher temperatures. The phases can then be characterized through the equation

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

where log K relates to a series of solutes on the same phase. The explanatory variables are solute parameters, R_2 an excess molar refraction, π_2^{H} the solute dipolarity–polarizability, $\Sigma\alpha_2^{\mathrm{H}}$ and $\Sigma\beta_2^{\mathrm{H}}$ the solute hydrogen bond acidity and basicity and log L^{16} where L^{16} is the K-value on hexadecane. The coefficients in the above equation then characterize the particular phase, the most important being s the phase dipolarity–polarizability, a the phase basicity, b the phase acidity and l a constant that reflects a combination of cavity effects and general dispersion interactions and is related to the ability of the phase to distinguish between homologues. Derivation of the constants for the various phases provides a quantitative method for the analysis of the selectivity of phases for particular solute analytes and a term-by-term investigation of log K values shows exactly the solubility interactions that lead to sorption of a solute by a phase and hence to the analytical determination of the solute through chemical microsensors.

The process of sorption plays a key role in the performance of chemical microsensors for gas phase analysis.[1] In general terms, such a microsensor consists of a physical transducer and a selective sorbent layer. The transducer does not directly detect the analyte molecules in the gase phase; instead, it senses changes in the physical properties of the sorbent layer on its surface. It is the sorption of analyte molecules from the gas phase into the sorbent layer and the consequent modification of the sensed properties of this layer, that results in the detection of the analyte molecules in the gase phase. This paper will focus on quantifying and understanding the absorption of organic vapours by polymeric materials that either have been, or could be used as selective sorbent layers (or as components of these layers) on chemical microsensors.

The response, Q, of a chemical microsensor is found empirically to be a function of the gas phase analyte concentration, C_{v}, eqn. (1). Indeed, sensor sensitivity is defined as

$$Q \propto C_{\mathrm{v}} \qquad (1)$$

the incremental change in signal that occurs in response to an incremental change in analyte concentration. From a mechanistic point of view, however, sensor response is actually a function of the concentration of analyte in the sorbent layer, C_{s}, eqn. (2). The concentrations of analyte in the gas and sorbent

$$Q = fC_{\mathrm{s}} \qquad (2)$$

phases are related through the partition coefficient, K, defined in eqn. (3). Then[1] from eqns. (2) and (3) eqn. (4) is obtained.

$$K = C_{\mathrm{s}}/C_{\mathrm{v}} \qquad (3)$$

$$Q = fKC_{\mathrm{v}} \qquad (4)$$

Eqn. (4) provides a very general relationship that illustrates the key role of sorption and of the partition coefficient in the response of a chemical sensor. Responses of surface acoustic wave (SAW) vapour sensors, for example, have been expressed in these terms.[2,3] It follows that an understanding of sorption and the factors that contribute to the selective sorption of analyte species, is central to the understanding of chemical microsensors for gas phase analysis.

In a previous review,[1] we set out an approach to understanding and investigating sorption phenomena as applied to chemical sensors. This approach is based on understanding the solvation properties of the vapours to be detected, the solubility properties of the sorbent layer phase and the various possible interactions between them. These will include dispersion interactions, dipole–induced-dipole interactions, dipole–dipole interactions and two types of hydrogen bond interactions (solute acid–solvent base and solute base–solvent acid). The properties of the analyte vapours, which can be regarded as solutes, are characterized by a set of solvation parameters or descriptors.[4–9] R_2 is an excess molar refraction that provides a quantitative indication of solute polarizable n- and p-electrons.[4] π_2^{H} is a dipolarity–polarizability parameter that measures the ability of a molecule to stabilize an external charge or dipole[5–7] and $\Sigma\alpha_{\mathrm{H}}^{2}$ and $\Sigma\beta_{\mathrm{H}}^{2}$ are the effective hydrogen bond acidities and basicities of the solute molecules.[8] The final parameter is log L^{16} where L (equivalent to K) is the Ostwald solubility coefficient on hexadecane at 298 K.[8] This parameter is a combination of exoergic dispersion interactions leading to an increase in the solubility of a solute (*i.e.* to an increase in L^{16}) and the endoergic cost of forming a cavity, leading to a decrease in L^{16}). These solvation parameters are now available for some 2000 organic molecules.[4–9]

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† For part 28, see ref. 41.

In order to apply these parameters to any given solvation process, partition coefficients (as log K values) are required for a range of solute molecules on a given solvent phase. The log K values are then correlated with the various parameters (*i.e.* those that are statistically significant) through the linear-solvation energy relationship (LSER) (5); where the coefficients

$$\log K = c + rR_2 + s\pi_2^{\mathrm{H}} + a\Sigma\alpha_2^{\mathrm{H}} + b\Sigma\beta_2^{\mathrm{H}} + l\log L^{16} \quad (5)$$

c, r, s, a, b and l are obtained through multiple linear-regression analysis. Provided that the variety of solutes studied covers suitable ranges of the descriptors, the coefficients in eqn. (5) will characterize the given solvent (or solvent phase) in terms of specific interactions. Thus r will relate to the ability of the phase to interact with solute n- and π-electrons and is an indicator of polarizability. Usually r is slightly positive, but can become negative if the phase contains a number of fluorine atoms. The s coefficient measures the dipolarity–polarizability of the solvent phase. The a coefficient measures the phase hydrogen bond basicity, this being the complimentary property to solute hydrogen bond acidity. Similarly, the b coefficient will measure the phase hydrogen bond acidity. The l coefficient is important in selective sorption, because it is a measure of the ability of a solvent phase to separate and to distinguish between, members of an homologous series.

The obtained LSER equation, based on eqn. (5), can be used in several ways. First, as just explained, the coefficients in eqn. (5) are characteristic constants of the solvent phase in question. Secondly, the value of log K for any given solute or analyte can be broken down into individual terms that show quantitatively the various solubility interactions that govern the overall solute solubility. Thirdly, further partition coefficients can be predicted for any solute or analyte whose solvation parameters are known.

Of course, other approaches to the understanding of solvation phenomena have been described. In the method of Poole *et al.*[10] the overall free energy of solvation of a solute, X [eqn. (6)] is divided into a cavity term, a non-polar term and a

$$\Delta G_{\mathrm{S}}^{\mathrm{SOLN}}(\mathrm{X}) = -RT\ln K(\mathrm{X}) \quad (6)$$

polar term [eqn. (7)]. Since the cavity term cannot be obtained

$$\Delta G_{\mathrm{S}}^{\mathrm{SOLN}}(\mathrm{X}) = \Delta G_{\mathrm{S}}^{\mathrm{CAV}}(\mathrm{X}) + \Delta G_{\mathrm{S}}^{\mathrm{NP}}(\mathrm{X}) + \Delta G_{\mathrm{S}}^{\mathrm{P}}(\mathrm{X}) \quad (7)$$

experimentally, a more useful division leads to eqn. (8), where

$$\Delta G_{\mathrm{S}}^{\mathrm{SOLN}}(\mathrm{X}) = \Delta G_{\mathrm{S}}^{\mathrm{CAV+DISP}}(\mathrm{X}) + \Delta G_{\mathrm{S}}^{\mathrm{INT}}(\mathrm{X}) \quad (8)$$

the combined cavity plus dispersion term can be obtained through measurements on a squalane liquid phase and the interaction term obtained by difference. Although eqns. (5) and (8) have been shown to be compatible,[11] eqn. (8) is not so useful from our point of view: it does not break down the overall interaction into component parts and since $\Delta G_{\mathrm{S}}^{\mathrm{INT}}(\mathrm{X})$ is obtained by difference, there is no way that any predictions of $\Delta G_{\mathrm{S}}^{\mathrm{SOLN}}(\mathrm{X})$ and hence of log K can be made.

The most widely used method of characterization of polymeric liquid phases is based on the Hildebrand–Scatchard theory of non-electrolytes in terms of the Hildebrand solubility parameter.[12] However, determination of the total solubility parameter for polymers is not easy and, in any case, the total parameter contains no information on the propensity of the polymers to undergo specific interactions. Partial solubility parameters have been introduced to remedy this, but they are approximate, they are limited to a restricted range of functionalities and, in particular, there is no distinction made between a hydrogen bond base and a hydrogen bond acid.[13,14]

Thus for our purpose, there is no practical alternative to the use of the general solvation equation, [eqn. (5)]. In the present work we shall apply this equation to log K values of a wide variety of solute type on given phases, usually soft organic materials such as polymers or oligomers above their T_g values. As we have demonstrated before, the simplest method of determining gas–liquid partition coefficients for a set of solutes on a given liquid phase is by GLC.[9] In the GLC method, the liquid phase in question is made up as the GLC stationary phase and precise measurements of the specific retention volume at the column temperature, V_g, lead through standard equations[9] to values of K.

Experimental

Materials.—Solutes were the best available commercial grades, used as such. Note that the GLC method does not require the use of pure solutes. The sorbent phases examined are listed in Table 1 with their abbreviations and their chemical structures are shown in Fig. 1. The SXPH samples are 75%-phenyl-25%-methylpolysiloxanes, obtained from Petrarch Systems (SXPHA) or as OV-25 from Phase Separations Ltd (SXPHB). The SXPHA column, modified by injections of trimethylchlorosilane is denoted SXPHC. These are the same phenylsiloxanes reported in ref. 15. OV-202 was obtained from Phase Separations Limited. SXCN was obtained from Petrarch Chemicals. SXPYR was a kind gift from Martel Zeldin and William Fife of the University of Indiana-Purdue University at Indianapolis, with a molecular weight of 3000–4000.[16] PVTD was prepared by the acid-catalysed reaction of poly(vinyl alcohol) and tetradecanal and is the same material reported in ref. 17 and 18. PIB was from Aldrich with a quoted average molecular weight of 380 000. PVPR was also from Aldrich; it was supplied as a solution in toluene and the solid polymer was obtained by rotary evaporation of the toluene, followed by removal of residual toluene as the azeotrope with ethanol. PECH, was from Aldrich. PEI was supplied as a solid by Phase Separations Limited. PEM was prepared by acid-catalysed polymerization of ethylene glycol and maleic anhydride as previously described.[19] P4V, was synthesized as reported in ref. 20. Z-DOL is a perfluoropolyether terminated with CF_2CH_2OH groups from Ausimont, with a reported average molecular weight of 2000. FPOL was a gift from Jim Griffith NRL Chemistry Division and is the same material we have used before.[2,3]

SXFA is a new polysiloxane material synthesized by the reaction of hexafluoroacetone with an allyl-substituted polysiloxane, taking advantage of the reactivity of perfluoroketones with terminal olefins as described by Urry *et al.*[21] To obtain the allyl-substituted polysiloxane, 10.8 g of methylallyldichlorosilane (Petrarch) were dissolved in 25 cm^3 of diethyl ether. 100 cm^3 of water were added, slowly at first (to control the boiling of the ether) and stirred for 5 h. Additional ether was added, the phases were separated and the polysiloxane was obtained from the ether phase (after drying with $MgSO_4$) by evaporation. Yield 6.93 g, theoretical, 6.97 g. IR spectra confirmed the formation of siloxane bridges, terminal Si–OH and the presence of the carbon–carbon double bond. Over a three week period dense droplets, assumed to be water, generated by the condensation of Si–OH groups separated from the material. The polysiloxane was taken up in ether, dried with $MgSO_4$ and the ether was evaporated. To this sample, 10 drops of 0.2 mol dm^{-3} phenyltrimethylammonium hydroxide in methanol were added and the sample was heated at 380–400 K for 1 h to catalyse chain lengthening. Finally a vacuum was applied to the hot sample to remove any volatiles. An IR spectrum confirmed that fewer Si–OH groups were present. 5 g of the poly(allyl)methylsiloxane were added to a glass-lined stainless steel Parr bomb

Table 1 Phases used, their abbreviations and columns

Phase	Abbr.	Phase density/g cm^{-3}	Support, mesh size	Solvent	Phase (%)	Packing wt/g	Column *l*/mm
Poly[oxy(methylphenylsilylene)-*co*-oxy(diphenylsilylene)], OV-25	SXPHA	1.150	GAW DMCS, 40–60	Propanone	9.99	1.5447 0.3232	72.0 14.0
Poly[oxy(methylphenylsilylene)-*co*-oxy(diphenylsilylene)], OV-25	SXPHB	1.150	GAW DMCS, 40–60	Propanone	9.99	1.5396	72.0
Poly[oxy(methylphenylsilylene)-*co*-oxy(diphenylsilylene)], modified	SXPHC	1.150	GAW DMCS, 40–60	Propanone	9.99	1.5447	72.0
Poly{oxy[methyl(3,3,3-trifluoroprop-1-yl)silylene]}, OV-202	OV-202	1.252	GAW DMCS, 40–60	Chloroform	9.99	2.9400	74.0
Poly{oxy[bis(3-cyanoprop-1-yl)silylene]}	SXCN	1.120	GAW DMCS, 40–60	Toluene	7.14	4.1613	105.0
Poly(oxy{methyl[4-hydroxy-4,4,bis(trifluoromethyl)but-1-en-1-yl]silylene})	SXFA	1.477	GAW DMCS, 40–60	Chloroform	10.00	2.9596	76.0
Poly(oxy{methyl[3-(*N*-methyl-*N*-4-pyridylamino)propyl]silylene})	SXPYR	(1.00)	GAW DMCS, 40–60	Chloroform	9.99	2.9220	73.5
Poly[(2-tridecyl-1,3-dioxolane-4,6-diyl)(2-hydroxypropane-1,3-diyl)]	PVTD	0.960	GAW DMCS, 40–60	Chloroform	9.99	3.1570	74.0
Poly(1,1-dimethylethylene)	PIB	0.918	GAW DMCS, 40–60	Hexane	6.55	5.6527	100.0
Poly(1-propionyloxyethylene)	PVPR	1.010	GAW DMCS, 40–60	Propanone	9.99	3.0160	74.0
Poly{oxy[1-(chloromethyl)ethylene]}	PECH	1.360	GAW DMCS, 40–60	Chloroform	7.58	1.3298	50.0
Poly(ethyleneimine)[a]	PEI	1.050	GAW DMCS, 40–60	Methanol	10.64	0.2951	18.0
Poly(oxymaleoyloxyethylene)	PEM	1.353	GAW DMCS, 60–80	Chloroform	4.11	0.2950	76.0
Poly{1-[4-(2-hydroxy-1,1,1,3,3,3-hexafluoroprop-2-yl)phenyl]ethylene}	P4V	1.444	GAW DMCS, 40–60	Methanol	3.74	0.5160	76.0
Fomblin Z-DOL[b]	ZDOL	1.80 (298 K), 1.73 (333 K)	GAW DMCS, 40–60	Propanone	10.00	3.4781	76.0
Fluoropolyol[c]	FPOL	1.653 (298 K), 1.604 (333 K)	GAW DMCS, 60–80	CH_2Cl_2	4.06	2.7094	72.0

[a] Poly(iminoethylene). [b] α-(1,1-Difluoro-2-hydroxyethyl)-ω-(oxy-1,1-difluoro-2-hydroxyethyl)-poly[oxy(difluoromethylene)-*co*-oxy(1,1,2,2-tetrafluoroethylene)]. [c] Poly{oxy[1,1,5,5-tetrakis(trifluoromethyl)pent-2-ene-1,5-diyl]oxy(2-hydroxypropane-1,3-diyl)oxy[bis(trifluoromethyl)methylene]-1,3-phenylene[bis(trifluoromethyl)methylene]oxy(2-hydroxypropane-1,3-diyl)}.

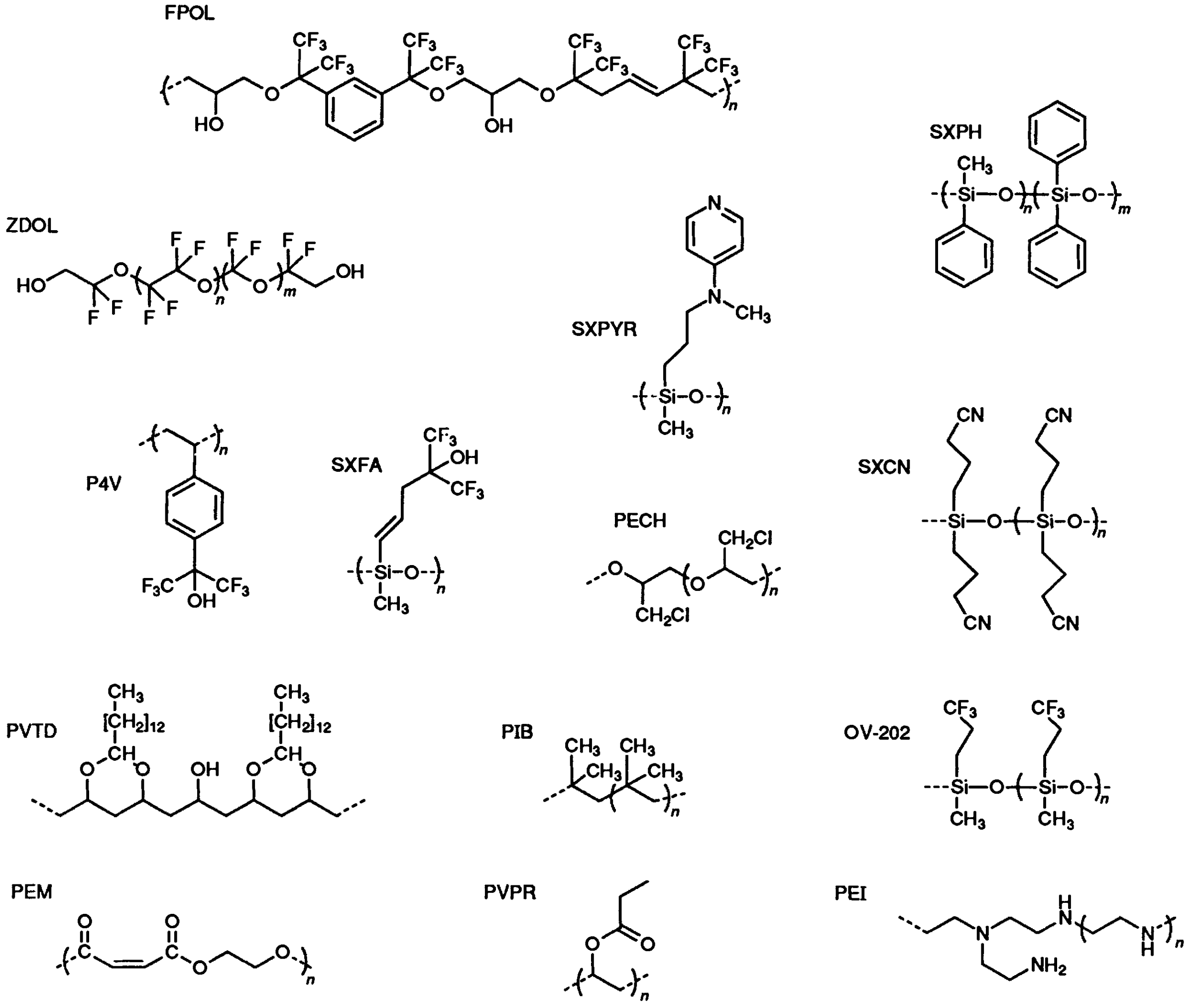

Fig. 1 Structural units of the sorbent phases examined in this study. In some cases, more than one repeat unit has been shown to illustrate structural characteristics or the chemical environment that a sorbed vapour would experience. The meanings of the name abbreviations can be found in Table 1.

and the sample was purged with nitrogen and evacuated. 33.3 g of gaseous hexafluoroacetone were added, which is approximately four times in excess relative to the allyl groups, assuming a 1 : 1 stoichiometry. The reaction temperature was raised to 370 K and held at 370–380 K for 43 h. After cooling, the excess hexafluoroacetone was recovered by vacuum transfer and weighed, (22.9 g). The 10.4 g hexafluoroacetone consumed compares with 8.3 g that would be consumed assuming a 1 : 1 stoichiometry with the allyl groups (*i.e.* 125% incorporation of hexafluoroacetone as 1,1,1,3,3,3-hexafluoropropan-2-ol groups based on apparent hexafluoroacetone consumption). Dry nitrogen was passed over the sample at 310 K overnight to drive off residual hexafluoroacetone and then the sample was evacuated for 1 h. The yield of polymer was 12.06 g, compared with a theoretical yield of 13.3 g for one hexafluoroacetone reacting with each allyl group. This indicates at least 84% incorporation of hexafluoroacetone as 1,1,1,3,3,3-hexafluoropropan-2-ol groups. From the two results, 125% incorporation based on hexafluoroacetone consumed and 84% based on the weight gain of the polymer and the known chemistry of hexafluoroacetone with olefins,[21] it was concluded that the sample contains *ca.* one 1,1,1,3,3,3-hexafluoropropan-2-ol group per monomer unit. The IR spectrum confirmed the presence of the hydroxy groups, new carbon fluorine bonds, disappearance of the allyl functionality and a new carbon–carbon double bond. The product is a viscous liquid whose density was measured in a calibrated tube: 1.48 g cm^{-3} at 298 K.

GLC Measurements.—All the phases were coated onto a Chromosorb support, from Phase Separations Ltd. Details of the solvents used in making up the stationary phases, the percentage of phase on the support, and the columns used are in Table 1. In most cases the percentage phase was obtained through direct weighing of the phase and the solid support prior to mixing with the solvent. Great care was taken to avoid any grease and the solvent was gently evaporated using a rotary evaporator with greaseless joints. Columns were weighed before and after packing and also from time to time to check that there was no weight loss during the experiments. In the case of SXPHA and SXPHB, weight percentages of the phase were also obtained by extraction of the dried coated support with acetone[15] and with PIB and PECH weight percentages were obtained by heating the dry coated support to constant weight in a crucible.

Retention data were obtained exactly as described before[9] and were corrected for the pressure drop across the column,[9] to yield retention volumes at the column temperature, V_g. The V_g values were converted into the required partition coefficients using the phase density at the column temperature; ρ_1 see Table 1, according to: K (or L) = $V_g \rho_1$. For SXPYR we have assumed a density of 1.00 in the calculation of K.

Note that any error in this procedure affects only the constant in eqn. (5). Details of the retention data obtained are in Table A,‡ except for FPOL which are given separately in Table 2 (because of the quite different solute set used in the FPOL experiments).

IR Measurements.—Fourier-transform IR (FTIR) spectra were taken on a Nicolet Model 205 FTIR spectrometer using potassium bromide discs with air reference. The spectrum of OV 202 was clear of any OH bands in the 3400 cm^{-1} region, PVTD showed a very large band due to associated OH at 3400 cm^{-1}, PVPR showed small bands due to unassociated OH near to 3400 cm^{-1} and ZDOL shows a large band at 3400 cm^{-1} due to associated OH. FTIR measurements of SXPH phases have already been reported.[15]

Results and Discussion

Although all the retention data have been corrected, as usual, for the pressure drop along the chromatographic column, they have not been analysed in terms of interfacial adsorption and so are uncorrected for any such effect. Poole *et al.*[10] have shown that interfacial adsorption can contribute significantly to the overall retention, especially for non-polar solutes such as the alkanes on polar phases. We have not carried out any such corrections, first, because these are not needed for the purpose of testing phases as possible microsensor coating (where interfacial adsorption will also contribute to retention) and secondly because of the lengthy and time-consuming procedure involved. However, we have analysed the data on polar phases both with and without results for alkanes and find almost no difference in the regression equations, so that we feel any contributions from interfacial adsorption will not markedly affect our results.

All the phases but one are either viscous liquids or rubbery solids above their glass transition temperature, T_g, and hence give rise to very broad chromatographic peaks at room temperature that are much more difficult to measure than usual. We therefore expect that the quality of the regression equations according to eqn. (5) will not be as good as with normal chromatographic phases at elevated temperatures.[4] In the event, application of eqn. (5) to the results listed in Tables A and 2 yields regression equations that range from excellent for SXPHA, OV-202, PVTD, PECH and ZDOL to rather poor for P4V especially. P4V is the only phase studied that is not above its glass transition temperature, T_g = 395 K, so that the poor correlation for P4V is not unexpected. The solute parameters used in the regression analysis are in Table B ‡ and details of the regression equations are collected in Table 3, where the coefficients in eqn. (5) are given together with *n* the number of solutes used, ρ the correlation coefficient, *sd* the overall standard deviation and *F* the Fisher *F*-statistic. Below each coefficient is the standard deviation in that coefficient. In all the regressions we checked for possible interrelations between the descriptors by calculating the cross-correlation coefficients. In a typical case, that of SXCN, the highest cross-correlation coefficients are those between R_2 and π_2^H (0.443) and between $\Sigma\alpha_2^H$ and log L^{16} (−0.498), with ρ^2 = 0.196 and 0.248, respectively. This example shows that with a suitable choice of solutes, it is possible to avoid difficulties over strong cross correlations of descriptors.

Because the LSER coefficients provide a measure of the properties of each sorbent phase, it is now possible to examine those properties in detail and to evaluate how chemical structure contributes to those properties. In our previous review, we had set out a number of organic functional groups

Table 2 Values of log *K* and log tREL for FPOL

Solute	log *K* (*T* = 298)	log *K* (*T* = 333)	log tREL (*T* = 393)
Octane	1.75	1.80	
2,2,4-Trimethylpentane	1.22	1.30	
Nonane	2.19	2.04	
Decane	2.66	2.36	
Hexadecane			0.00
Octadecane			0.38
Dichloromethane	1.42	1.27	
Trichloromethane	1.39	1.53	
Tetrachloromethane	1.26	1.58	
1,2-Dichloroethane	1.94	1.82	
2-Methyl-2-chloropropane	1.66	1.56	
Dioxane		3.34	
Acetaldehyde	2.33	2.06	
Heptanal			−0.13
Propanone	3.21	2.65	
Butanone	3.66	2.87	
Nonan-2-one			0.12
Nonan-5-one			−0.01
2,6-Dimethylheptan-4-one			−0.34
Decan-2-one			0.34
Cyclopentanone	4.54	3.69	
Cyclohexanone			−0.06
Ethyl formate	2.55	2.15	
Methyl acetate	2.89	2.43	
Ethyl acetate	3.26	2.72	
Propyl acetate	3.75	3.02	
Pentyl acetate			−0.53
Acetonitrile	3.11	2.59	
Ethylamine		2.66	
Nitromethane	2.85	2.40	
Nitroethane	3.16	2.68	
Dimethylacetamide		5.46	
Methanol	2.76	2.23	
Ethanol	2.86	2.39	
Propan-1-ol	3.34	2.65	
Butan-1-ol	3.84	2.98	
Pentan-1-ol		3.31	
Hexan-1-ol		3.62	
Heptan-1-ol			−0.27
Heptan-4-ol			−0.59
Octan-1-ol			−0.06
Octan-2-ol			−0.26
Decan-1-ol			0.34
Cyclohexanol			−0.30
2-Methoxyethanol			−0.56
Toluene	2.37	2.29	
Methyl phenyl ether	3.88	3.08	
2,6-Dimethylanisole			−0.43
Diphenyl ether			0.32
1,2-Dimethoxybenzene			0.24
1,3-Dimethoxybenzene			0.19
1,4-Dimethoxybenzene			0.12
Methyl benzoate			0.09
Benzonitrile			−0.06
Nitrobenzene			0.02
Phenol			−0.32
o-Cresol			−0.21
m-Cresol			−0.05
p-Cresol			0.07
3-Ethylphenol			0.12
2-Isopropylphenol			−0.02
3-Isopropylphenol			0.24
4-Butylphenol			0.53
4-Fluorophenol			0.13
3-Chlorophenol			0.18
3-Cyanophenol			1.30
3-Nitrophenol			1.38
4-Nitrophenol			1.67
Benzyl alcohol			0.11

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‡ Tables A and B are available as supplementary material from the authors. They have also been deposited under the Supplementary Publications Scheme. For details of the Scheme see 'Instructions for Authors (1994)', *J. Chem. Soc., Perkin Trans. 2*, 1994, issue 1 [Supp. Pub. No. 57054 (13 pp)].

Table 3 Correlations using eqn. (5)

Phase *T*/K	*c*	*r*	*s*	*a*	*b*	*l*	*n*
SXPHA 298	−0.452	0.308	0.851	0.692	1.297	0.806	72
	0.051	0.055	0.067	0.073	0.070	0.011	
SXPHB 298	−0.846	0.177	1.287	0.556	0.440	0.885	40
	0.076	0.080	0.081	0.085	0.084	0.019	
SXPHC 298	−2.949	0.246	0.992	0.549	0.827	0.794	23
	0.116	0.114	0.102	0.120	0.117	0.033	
OV202	−0.391	−0.480	1.298	0.441	0.705	0.807	50
	0.047	0.061	0.063	0.070	0.055	0.013	
SXCN 298	−1.630	0.000	2.283	3.032	0.516	0.773	52
	0.076	0.087	0.101	0.117	0.101	0.016	
SXCN 343	(−3.601)	0.280	1.518	2.110	0.460	0.555	52
	0.104	0.108	0.143	0.111	0.153	0.021	
SXFA 298	−0.084	−0.417	0.602	0.698	4.250	0.718	36
	0.118	0.114	0.115	0.135	0.136	0.032	
SXPYR 298	−1.938	−0.189	2.425	6.780		1.016	39
	0.128	0.112	0.117	0.220		0.034	
PVTD 298	−0.591	−0.016	0.736	2.436	0.224	0.919	42
	0.060	0.068	0.069	0.071	0.071	0.016	
PIB 298	−0.766	−0.077	0.366	0.180		1.016	36
	0.059	0.068	0.044	0.086		0.017	
PVPR 298	−0.571	0.674	0.828	2.246	1.026	0.718	33
	0.078	0.081	0.089	0.095	0.100	0.019	
PECH 298	−0.749	0.096	1.628	1.450	0.707	0.831	50
	0.054	0.049	0.059	0.065	0.057	0.011	
PEI 298	−1.602	0.495	1.516	7.018		0.770	51
	0.108	0.096	0.100	0.203		0.024	
PEM 298	−1.653	−1.032	2.754	4.226		0.865	31
	0.167	0.237	0.154	0.293		0.038	
P4V 298	−1.329	−1.538	2.493	1.507	5.877	0.904	26
	0.494	0.481	0.525	0.716	0.665	0.109	
P4V 333	(−4.279)	−0.855	1.698	1.157	4.321	0.683	25
	0.368	0.249	0.253	0.337	0.434	0.064	
ZDOL 298	−0.486	−0.750	0.606	1.441	3.668	0.709	46
	0.059	0.065	0.071	0.083	0.085	0.013	
ZDOL 333	−0.450	−0.731	0.831	0.759	2.719	0.562	47
	0.055	0.046	0.067	0.059	0.069	0.008	
FPOL 298	−1.207	−0.672	1.446	1.494	4.086	0.810	26
	0.187	0.255	0.231	0.328	0.257	0.058	
FPOL 333	−0.527	−0.464	1.152	0.908	2.645	0.611	31
	0.116	0.200	0.156	0.223	0.180	0.031	
FPOL 393	(−3.015)	−0.634	1.374	0.614	0.877	0.386	38
	0.188	0.095	0.091	0.075	0.165	0.024	

expected to confer particular properties to sorbent phases.[1] These expectations can now be examined. If a particular coefficient is very large, then any solute with a complementary solubility property will be sorbed. For example, if the *a* coefficient is large then solutes that are hydrogen bond acids will be sorbed and the phase itself is hydrogen bond base. For selectivity, it is desirable that in addition to a large coefficient for the interaction of interest, the other coefficients in the regression should be relatively small. In practice, most materials will interact by multiple interactions, so selectivity is a matter of degree. To maximize sorption and thus the sensitivity of a sensor for detection of vapours at trace concentrations, all favourable interactions should be large so that the interaction terms plus the constant add up to a large partition coefficient.

For selectivity in the sorption of basic vapours, a phase should be hydrogen bond acidic, and alcohol or phenol groups with fluoro-substitution are expected to confer this property.[1] Fluoro-substitution increases the acidity and decreases the basicity of the hydroxy group. A series of phenolic phases were examined in a previous study and the fluoro-substituted phenol was the most acidic of these.[22] Four fluoroalcohol-containing phases were examined in this study: FPOL, P4V, SXFA and ZDOL. All are strong hydrogen bond acids, as indicated by their large *b* coefficients of 4.086, 5.877, 4.25 and 3.668, respectively. P4V is one of a series of fluoroalcohol-containing phases examined by Snow *et al.* as selective layers on SAW device.[20] Polymers similar to P4V were first suggested for sensor applications by Barlow and co-workers.[23,24] FPOL is an oligomer that has proved useful in chemical sensor studies for the detection of basic compounds such as phosphonates.[2,20,25–27] SXFA was synthesized with the aim of incorporating the 1,1,1,3,3,3-hexafluoropropan-2-ol group into a siloxane polymer. Polysiloxanes are generally liquid or rubbery polymers at room temperature. ZDOL is a commercial liquid.

Of these four, P4V has the largest *b* coefficient (5.877), but this polymer has a rather high glass transition temperature of 395 K,[20] so vapours diffuse through it rather slowly. SXFA has the next highest *b* coefficient (4.25), is a viscous liquid at room temperature and should be quite selective for bases. All its other coefficients are comparatively small. FPOL will be somewhat less selective, since it also has a significant *s* coefficient for dipolarity–polarizability and weak basicity. However, the dipolarity of this phase, in combination with its acidity, should increase the strength with which it sorbs dipolar basic vapours (*e.g.* phosphonates) and hence yield sensors with high sensitivity. The phase ZDOL is slightly less acidic (*s* = 3.668) than the other fluoroalcohol-containing materials in this study. Its hydroxy groups only occur at the chain ends, yet is still has considerable acidity, indicating that functional groups limited to chain ends can have a significant effect on material properties.

One additional phase in our data set, PVTD, contains hydroxy groups in its structure and might be expected to be a hydrogen bond acid. Although the aliphatic alcohols are less acidic than fluoro-substituted alcohols, the b coefficient of PVTD was unexpectedly small at 0.224. The FTIR spectrum of this material showed the hydroxy groups as a broad band indicating that they are associated and this result together with the regression analysis suggests that internal hydrogen bonding is occurring. This reduces the availability of the acidic hydrogens to external hydrogen bond basic vapours. PVTD is basic with $a = 2.436$, as expected for a hydroxy group containing phase and this basicity may be enhanced by the internal hydrogen bonding, since the OH oxygen in the complex –OH • • • O will become more basic towards external acids. PVTD does not have any particular selectivity as a sorbent phase, but comparison of its regression results with those of the more acidic phases discussed above confirms the value and importance of fluoro-substitution for obtaining acidic properties from the hydroxy groups of alcohols.

Hydrogen bond basicity in a phase promotes the sorption of hydrogen bond acidic vapours such as alcohols and water. Basicity is maximized in PEI and SXPYR. PEI was selected for study because it contains alkylamine functionalities that should confer basicity with minimum dipolarity and negligible hydrogen bond acidity.[1] In addition, PEI has been used in chemical sensor studies.[27,28] The quite large a coefficient (7.018) of PEI confirms its basicity, but the moderate s coefficient of 1.516 is somewhat larger than expected. This may be a consequence of quaternized ammonium groups common in commercial samples of PEI, which could give rise to charge–dipole interactions. The SXPYR phase contains alkylaminopyridyl groups expected to be quite basic.[29] In the polymer, they are indeed quite basic, as indicated by the large a coefficient of 6.78. The observed s coefficient of 2.425 for dipolarity–polarizability is consistent with the large dipolarity of the 4-(N,N-dimethylamino)pyridine, whose dipole moment is 4.33 D.[30]

In terms of selectivity for dipolarity, trade-offs between dipolarity and basicity must be made.[1] The OV-202 offers moderate dipolarity, as expected from the polarizing effect of the trifluoropropyl groups and confirmed experimentally by its s coefficient of 1.298. At the same time it has no appreciable basicity. More strongly dipolar groups are invariably basic. In our review, we selected cyano-substitution as a means of obtaining strong dipolarity with only moderate basicity.[1] The s coefficient (2.283) of SXCN confirms that it is one of the most dipolar of the phases studied, while the a coefficient of 3.032 is less than half those of the more strongly basic phases PEI and SXPYR. The phase with the largest s coefficient is PEM (s = 2.754); this ester-containing phase is also somewhat more basic (a = 4.226) than SXCN. Simple organic esters are generally of only moderate dipolarity and moderate basicity and the s and a coefficients for PVPR (0.828 and 2.246, respectively) are more in keeping with these expectations. The larger s coefficient for PEM must be a consequence of the pair of ester groups conjugated with the carbon–carbon double bond in the maleate portion of the repeat unit. It was surprising that PVPR should exhibit hydrogen bond acidity (b = 1.026), as there are no acidic groups in its repeat unit. However, the IR spectrum of this phase revealed the presence of small bands due to hydroxy groups at 3600 cm^{-1}, indicating that the actual sample of material characterized does contain acidic groups in its structure. In any case, even without the hydrogen bond acidity, PVPR has no outstanding qualities as a selective phase. The OV-202 also exhibits slight hydrogen bond acidity (b = 0.705), which was unexpected. The IR spectrum confirmed that hydroxy groups were not detectable, but it is possible that the weak acidity arises from CH groups activated by adjacent trifluoromethyl groups. It is always possible that solute interactions with the support itself may lead to an apparent phase acidity. However, a quite large loading (9.99%) of OV-202 was used and with other phases such as PIB no acidity was found. One additional phase with a significant s coefficient (1.628) is PECH. Dipolarity in this material must arise from the polarizing effects of the electron-withdrawing Cl and O atoms. The ether linkages also give rise to weak basicity, a = 1.45. PECH does not have great selectivity, but it is a general sorbent for vapours of weak to moderate 'polarity' that has been used in chemical sensor studies.[13,25,27]

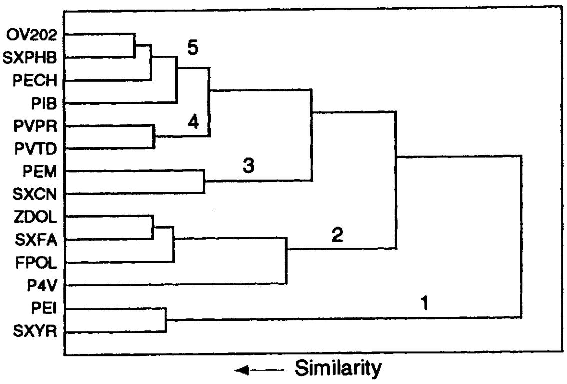

Fig. 2 Dendrogram illustrating the similarities and dissimilarities among the sorbent phases at 298 K, as determined by cluster analysis of the c constants and r, s, a, b and l coefficients

The remaining phases, SXPH and PIB, are non-polar phases that interact primarily by dispersion interactions. The SXPH materials were examined in the hope that the phenyl groups would render them particularly polarizable.[15] Although these materials do have more positive r and s coefficients than PIB, the effect is not large. The synthesis or identification of a more polarizable phase must await further study. The SXPH samples also exhibit weak hydrogen bond acidity as a consequence of hydroxy groups detectable by IR.[15] PIB is a simple aliphatic material and can only interact by dispersion interactions. It has one of the largest l coefficients in the data set. This coefficient is related to dispersion interactions that favour sorption and cavity-forming effects that disfavour sorption (since solvent–solvent interactions must be broken). In chromatographic studies, the larger the l coefficient, the better the separation of homologous vapours. Generally, homologues vary only by their capacity for dispersion interactions, all other interactions remaining similar in the series. In non-polar phases such as PIB, the cost of forming a cavity is expected to be less than in more polar phases where solvent–solvent interactions are stronger. In practice, PIB-coated sensors are more selective for hydrocarbons than are other sensors with more polar polymer coatings.[27]

Similarities and dissimilarities among the phases in this study can be seen visually in the dendrogram in Fig. 2. The first group at the bottom includes the two very basic phases, PEI and SXPYR, which are similar to one another and very dissimilar to all other phases. The second group contains the hydrogen bond acidic phases P4V, FPOL, SXFA and ZDOL. P4V, with the larger regression coefficients for acidity and dipolarity, is the most distinct among these, while SXFA and ZDOL are the most similar. SXFA and ZDOL are both selective acidic phases: their b coefficients are large while their s coefficients and a coefficients are relatively small. The phases in the third group, SXCN and PEM, are very dipolar phases that are moderately basic. The phases in the fourth group, PVTD and PVPR, are moderately basic phases, but are also weak acids. Finally, the remaining four phases, PIB, PECH, SXPHB and OV-202, are those with the least basicity and acidity and are in general less 'polar' than the others. Of these four, PIB is most distinct as it only undergoes dispersion interactions and has the largest *l* coefficient. The other three have moderate *s* coefficients. Cluster analysis displayed by dendrograms has been previously reported for deducing the properties of chemical sensor phases on the basis of chemical sensor responses[25] and for selecting among various phases based on chemical sensor responses.[31]

Given the coefficients for the sorbent phases and the solvation parameters for solute vapours, the individual terms in eqn. (5) can be calculated to quantify the individual interactions that govern the sorption process. The phases OV-202, SXFA and PEI are slective for dipolar, hydrogen bond basic and hydrogen bond acidic vapours, respectively. Nitromethane is a dipolar vapour with only moderate hydrogen bond basicity, 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) is strongly acidic, but of only moderate dipolarity–polarizability and limited basicity, whilst ethylamine is strongly basic. The solvation parameters for these compounds are listed in Table 4 and a detailed term-by-term analysis of their solubilities as log *K* in the three selective phases is given in Table 5. The phase OV-202 sorbs nitromethane most strongly, the deciding factor being $s\pi_2^H$ for dipolar interactions. SXFA selectively sorbs the base ethylamine with the significant term being $b\Sigma\beta_2^H$, whilst the very strong basic phase PEI selectively sorbs HFIP, the relevant term being $a\Sigma\alpha_2^H$. Such an analysis can be carried out for all the solutes in Table 4 on all the 14 characterized phases in order to assess the selectivities for particular vapours in detail.

In all the cases in Table 5 (and any others one may wish to consider) the $l \log L^{16}$ term contributes significantly to the overall sorption, but does not have a large effect on the selectivity among these three vapours. In general, dispersion interactions always occur in the sorption of an organic vapour, and these are not particularly selective, except that vapours with larger L^{16} values will be more strongly sorbed than those with smaller L^{16} values. In practice, this means that vapours from less volatile liquids will be more strongly sorbed and hence more easily sensed, than those from more volatile liquids, all other things being equal. If the selectivity of a sensor is determined primarily by the degree of sorption, there being no further selectivity contributed by the transduction mechanism, then it will be easier to detect vapours from liquids of low volatility, especially those with the additional possibility of participating in strong dipolar or acid–base interactions.

Since it is difficult to obtain an individual chemical microsensor that is completely selective under all conditions, sensors have been employed in arrays and their data analysed by pattern recognition techniques.[25,27,32–38] This method can greatly increase selectivity. As we set out in our review[1] the greatest amount of chemical information will be obtained from an array if each sensor in the array probes a different solubility interaction. The characterization of the sorbent phases according to eqn. (5), is given in Table 3, and the classification of these phases in Fig. 2, permits the clear identification of sorbent phases with particular properties and arrays of phases wherein each probes a different solute property.

It is also possible to derive LSER equations from the responses of polymer-coated SAW vapour sensors; this approach has been used recently by Patrash and Zellers for a set of four such phases.[39] In this case, the LSER equations do not predict thermodynamic position coefficients, *K*, but they predict a parameter that was first denoted as *KSAW* by Grate and co-workers[2,3] and subsequently as *Ke* by Patrash and Zellers.[39] *KSAW* is related to *K*, but is not identical to it because the response of a SAW sensor is not necessarily simply a function of the mass of vapour sorbed.[3]

Temperature Studies.—Although we were primarily concerned with the determination of log *K* values at ambient temperature, at which microsensors are usually operated, we thought it useful to carry out a few measurements at other temperatures. We chose SXCN (298 and 343), ZDOL (298 and 333) and FPOL (298, 333 and 393 K) as examples and collect the regression coefficients in Table 6. Since some of these results are derived from measurements of relative retention, the *c* constants are omitted. For comparison, Table 6 also includes regression results calculated for the monomeric liquid *N*-formylmorpholine (NFM) using recent solvation parameters and data from our previous study.[40] Also in Table 6 are results for the acidic phase bis(3-allyl-4-hydroxyphenyl)sulfone, denoted as H10,[22] that we have recently re-investigated.[41] In general, the *s*, *a*, *b* and *l* coefficients all decrease with increasing temperature for both the polymeric and non-polymeric phases. These decreases can be quite large, so comparisons of one phase with another must refer to the same temperature. As we have noted previously,[2] log *K* values for individual compounds on a given phase decrease significantly with temperature. Thus for ZDOL, the average decrease in log K for 21 compounds from 298 to 333 K is 0.78 log units, corresponding to a decrease by a

Table 4 Solvation parameters for solutes of widely different functionalities

Solute	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	$\log L^{16}$
Nitromethane	0.313	0.95	0.06	0.31	1.892
HFIP	−0.240	0.55	0.77	0.10	1.392
Ethylamine	0.236	0.35	0.16	0.61	1.677

Table 5 Analysis of selective sorption at 298 K

							Total	
System	c	rR_2	$s\pi_2^H$	$a\Sigma\alpha_2^H$	$b\Sigma\beta_2^H$	$\log L^{16}$	Calc.	Obs.
OV-202								
Nitromethane	−0.391	−0.150	1.233	0.026	0.219	1.527	2.46	
HFIP	−0.391	0.115	0.714	0.340	0.071	1.123	1.97	1.99
Ethylamine	−0.391	−0.113	0.454	0.070	0.430	1.353	1.80	
SXFA								
Nitromethane	−0.084	−0.131	0.571	0.042	1.318	1.358	3.07	3.05
HFIP	−0.084	0.100	0.331	0.537	0.425	0.999	2.31	2.31
Ethylamine	−0.084	−0.098	0.210	0.117	2.593	1.204	3.94	
PEI								
Nitromethane	−1.602	0.155	1.440	0.421	0.000	1.457	1.87	
HFIP	−1.602	−0.119	0.834	5.404	0.000	1.072	5.59	
Ethylamine	−1.602	0.117	0.531	1.122	0.000	1.291	1.46	

Table 6 Regression coefficients for phases at different temperatures

		Coefficient					
Phase	*T*/K	*c*	*r*	*s*	*a*	*b*	*l*
SXCN	298	−1.63	0.00	2.28	3.03	0.52	0.773
	343	—	0.28	1.52	2.11	0.46	0.555
ZDOL	298	−0.49	−0.74	0.61	1.44	3.67	0.710
	333	−0.45	−0.73	0.81	0.76	2.72	0.560
FPOL	298	−1.21	−0.67	1.45	1.49	4.09	0.810
	333	−0.53	−0.46	1.15	0.91	2.65	0.611
	393	—	−0.63	1.37	0.61	0.88	0.386
NFM[a]	298	−0.52	0.03	2.55	4.30	0.00	0.724
	313	−0.53	0.06	2.37	3.88	0.00	0.667
	332	−0.55	0.08	2.15	3.40	0.00	0.600
	352	−0.57	0.10	1.97	2.97	0.00	0.539
	373	−0.57	0.13	1.78	2.55	0.00	0.485
H10[b]	394	−0.57	−0.05	1.32	1.27	1.46	0.418
	449	−0.75	0.16	1.16	0.81	1.29	0.332

[a] *N*-Formylmorpholine.[40] [b] Bis(3-allyl-4-hydroxyphenyl)sulfone.[41]

factor of six. This by iself would result in the sensitivity of a microsensor coated with ZDOL to be reduced by the same factor over the 35 °C temperature range.

ZDOL is one of the few commercially available phases that are strong hydrogen bond acids and so we thought it useful to study ZDOL in a little more detail, particularly as regards stability. We therefore repeated absolute measurements of log *K* values at 298 K after working with the same column at 333 K for some time. We found no decrease in the observed retention times, as would have been found if ZDOL had been lost from the column and conclude that ZDOL can be used at 333 K, at least, without loss owing to bleeding from the column.

The temperature studies on FPOL are interesting because of the collapse of the phase hydrogen bond acidity at 393 K. However, we are inclined to believe that this is due to some chemical alteration of the structure of FPOL at elevated temperature. Subsequent measurements at 298 K, after the phase had been used at 393 K, yielded log *K* values that led to a regression equation with a considerably reduced *b* coefficient compared with that obtained from measurements made before use at 393 K. The log *K* values at 298 and 333 K reported in Table 2 were all determined prior to use of the phase at 393 K. In any event, it is clear that FPOL at 393 K does not behave as a very acidic phase (compare the *b* coefficient of 0.88 with the *b* coefficient of 1.46 for the phenolic phase H10, at 394 K).

Conclusions

Gas–liquid partition coefficients that are critical in the evaluation of phases for chemical microsensors[1] can be obtained for a variety of analyte solutes on a given phase by gas chromatography. If some 20–30 values of log *K* are thus obtained for solutes with varying functional groups, the general solvation eqn. (5) can be applied to yield quantitative information on the selectivity and general solution properties of the phase concerned. In this way, we have studied 14 candidate phases with diverse chemical structures and have been able to choose phases that are selective towards dipolar–polarizable analytes, analytes that are hydrogen bond acids and analytes that are hydrogen bond bases. In this way, eqn. (5) provides a unifying principle for the selection and design of phases for chemical microsensors.

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