Short Communication

Hydrogen bonding

XIX. The characterisation of two poly(methylphenylsiloxane)s

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ABSTRACT

Two commercial samples of poly(methylphenylsiloxane) were characterised using our solvation equation,

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

where L is the gas–liquid partition coefficient for a series of solutes on a given stationary phase, and the explanatory variables are R_2 an excess molar refraction, π_2^H the solute dipolarity/polarisability, 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. For both samples, a substantial b- constant was found, *viz.* 1.22 ± 0.07 and 0.49 ± 0.08 at 25°C, suggesting that they can act as hydrogen-bond acid (contrary to their chemical formulation). Examination of the bulk liquid stationary phases by IR showed the presence of OH groups and confirmed our analysis by the solvation equation. It is suggested that workers using the OV or SE series of siloxanes routinely check the bulk stationary phases by IR in order to assess the presence or absence of OH groups.

INTRODUCTION

Poly(methylsiloxanes) and poly(methylphenylsiloxanes), especially as the OV and SE series, are amongst the most common stationary gas–liquid chromatography phases, both as regards general analytical applications and more fundamental physico-chemical studies [1–5]. As part of our studies on solute–solvent interactions, we were interested in a liquid phase in which large dispersion interactions might be set up. Of the various poly(methylphenylsiloxanes), OV-25, which is a poly(diphenylphenylmethylsiloxane) with 75% phenyl substitution, seemed the most likely candidate for such a phase. Our method of characterising liquid phases, and of identifying solute–solvent interactions has been set out in detail before [6–8]. Retention data are obtained for a series of solutes on a given phase at a given

temperature. These solute data, SP, can be specific retention volumes either at the column temperature, V_G, or corrected to $0°C$, V_G^0, or they can be gas–liquid partition coefficients, L, or even relative retention times, t. Values of log SP for a series of solutes are then regressed against various solute parameters as explanatory variables through the multiple linear regression eqn. 1. These solute parameters are R_2 an excess solute molar volume [9], π_2^H our new solute dipolarity/polarisability parameter [7], α_2^H and β_2^H the solute hydrogen-bond acidity and basicity (more correctly these are effective or summation values, $\sum\alpha_2^H$ and $\sum\beta_2^H$ [7]), and log L^{16} where L^{16} is the solute gas–liquid partition coefficient on hexadecane at $25°C$ [10].

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

The constants in eqn. 1 are found by multiple linear regression analysis and serve to characterise the stationary phase as follows: r is the tendency of the phase to interact with solute π- and n-electron pairs, s is the phase dipolarity/polarisability, a is the phase hydrogen-bond basicity (because basic phases will interact with acidic solutes), b is the phase hydrogen-bond acidity, and l is an important constant that indicates how well the phase will separate homologues in any homologous series [6]. Each term in eqn. 1 thus corresponds to a specific solute–solvent interaction. We expected that OV-25 would give rise to rather large r- and s-constants due to the phenyl groups in the siloxane, to a small a-constant because OV-25 will be slightly basic, and to a zero b constant because the phase will not be a hydrogen-bond acid at all.

EXPERIMENTAL

Gas–liquid partition coefficients were obtained in the usual way [10] at $25°C$; in the calculation of L values we took the density of the stationary phase as 1.15 g cm^3. Two samples were used. One from Petrach Chemicals we denote as SXPHA and one from Phase Separations we denote as SXPHB. In addition, we obtained relative retention times on an SXPHA column, modified by successive injections of trimethylchlorosilane: this column we denote as SXPHC. Stationary phases were coated onto Chromosorb GAW DMCS, 40–60 mesh, and column loadings were obtained by carefully weighing the stationary phase and the support into grease-free vessels prior to addition of acetone solvent, followed by careful evaporation. In addition, the dried coated support was extracted by acetone, and the residual support filtered off through a pre-weighed glass sinter. A blank experiment using an uncoated sample of inert support was run as a check. Column loadings by the original direct method were 9.99% on SXPHA and 9.93% on SXPHB. The extraction method gave loadings of 9.06% on SXPHA and 8.66% on SXPHB. Since the extractive method leads to the minimum loading, we have used the direct loadings in the calculation of L values. Use of the (lower) extraction method values would lead to log L values larger by 0.04 units on SXPHA and by 0.06 units on SXPHB. These would simply alter the c constant in the general eqn. 1 by the same amount. All results are collected in Table I.

Bulk samples of SXPHA and SXPHB were examined by IR as films between sodium chloride plates in the usual way.

$$\log L\text{(SXPHA)} = -0.48 + 0.22R_2 + 0.95\pi_2^H + 0.70\alpha_2^H + 1.22\beta_2^H + 0.815 \log L^{16} \quad (2)$$
$$\qquad\qquad\quad (0.06) \quad (0.06) \qquad (0.07) \qquad (0.09) \qquad (0.07) \qquad (0.014)$$
$$n = 78 \quad R = 0.9928 \quad \text{S.D.} = 0.12$$

$$\log L\text{(SXPHB)} = -0.79 + 0.24R_2 + 1.23\pi_2^H + 0.63\alpha_2^H + 0.49\beta_2^H + 0.866 \log L^{16} \quad (3)$$
$$\qquad\qquad\quad (0.08) \quad (0.08) \qquad (0.08) \qquad (0.09) \qquad (0.08) \qquad (0.020)$$
$$n = 42 \quad R = 0.9932 \quad \text{S.D.} = 0.10$$

$$\log t\text{(SXPHC)} = -2.96 + 0.21R_2 + 1.03\pi_2^H + 0.61\alpha_2^H + 0.79\beta_2^H + 0.800 \log L^{16} \quad (4)$$
$$\qquad\qquad\quad (0.10) \quad (0.10) \qquad (0.09) \qquad (0.11) \qquad (0.10) \qquad (0.030)$$
$$n = 24 \quad R = 0.9923 \quad \text{S.D.} = 0.09$$

TABLE 1

VALUES OF LOG L OR LOG t ON POLY(METHYLPHENYLSILOXANE) COLUMNS AT 25°C

Compound	Log L (SXPHA)	Log L (SXPHB)	Log t (SXPHC)	Compound	Log L (SXPHA)	Log L (SXPHB)	Log t (SXPHC)
Pentane			−1.13	Butyl propanoate	3.84	3.53	
Hexane	1.52	1.38	−0.86	Methyl trimethyl-	2.69		
Heptane	2.02	1.92	−0.48	acetate			
Octane	2.51	2.37	0.00	Acetonitrile		2.16	
Nonane	2.93	2.90		Triethylamine	3.49		
Decane	3.39	3.37	0.86	Nitromethane	2.55	2.40	−0.10
Undecane	3.81			Nitroethane	2.90	2.78	0.30
Dodecane	4.05			Methanol	1.82	1.42	−0.90
Tetradecane	4.98			Ethanol	2.15		−0.59
Cyclohexane	1.86			Propan-1-ol	2.58	2.03	−0.18
Dichloromethane	1.98	1.93		Propan-2-ol	2.24		
Trichloromethane	2.32	2.24		Butan-1-ol	3.01	2.53	0.28
Tetrachloromethane	2.30	2.19		2-Methylpropan-1-ol	2.67	2.31	−0.05
1,1-Dichloroethane	2.09			Butan-2-ol	2.67		
1,2-Dichloroethane	2.60			2-Methylpropan-2-ol	2.12	1.64	−0.54
1,1,2,2-Tetrachloro-	3.87			Pentan-1-ol	3.43	2.98	
ethane				Hexan-1-ol	3.86	3.45	
1-Chlorobutane	2.31	2.21		Heptan-1-ol	4.28	3.87	
1-Chloropentane	2.78	2.66		Octan-1-ol	4.64		
1,5-Dichloropentane	4.33			Trifluoroethanol	1.60	1.34	−1.02
Trichloroethene	2.56			Hexafluoropropan-2-ol	1.53	1.36	−0.86
Tetrachloroethene	3.06			Benzene	2.51	2.45	0.00
Dibromomethane	2.91			Toluene	3.00	2.92	0.40
1-Bromobutane	2.75	2.67		Ethylbenzene	3.39		
1-Bromooctane	4.34			o-Xylene	3.52	3.46	
Diethyl ether	1.97	1.43	−0.83	Propylbenzene	3.71		
Di-n-butyl ether	3.36	3.12	0.75	Butylbenzene	4.13	4.11	
1,4-Dioxane		2.85	0.66	1,2,3,4-Tetramethyl-	4.63		
Propanone	2.29	1.82	−0.39	benzene			
Butanone	2.69	2.28		Phenylethyne	3.58		
Pentan-2-one	3.01	2.67		Chlorobenzene	3.37		
Pentan-3-one	3.03			1,2-Dichlorobenzene	4.19		
Heptan-2-one	3.89	3.57		1,4-Dichlorobenzene	4.16		
Octan-2-one	4.26	3.99		2-Chlorotoluene	3.81	3.77	
Nonan-2-one	4.67			Bromobenzene	3.76	3.78	1.27
Cyclohexanone	4.21			Methylphenyl ether	3.87		
Methyl formate	1.60			Acetophenone	4.90		
Ethyl formate		1.82	−0.56	Methylbenzyl ketone	5.19		
Propyl formate	2.50			Methyl benzoate	4.86		
Butyl formate	2.95	2.71		Aniline	4.51		
Methyl acetate	2.27			N,N-Dimethylaniline	4.67		
Pentyl acetate	3.64			Pyrrole	3.30		
Ethyl propanoate	3.05	2.69	0.38				

RESULTS AND DISCUSSION

For the first commercial sample, denoted as SXPHA, we have log L values for 78 solutes at 25°C. We chose 25°C as the standard temperature so that in future we can compare results with those for numerous liquid phases that we are at present investigating. The various solute parameters were taken from our previous compilation [7]. Although we expected the b constant in eqn. 1 to be zero, we first regressed the log L values against all five solute parameters as a matter of course. We were thus very surprised to obtain eqn. 2. Here, the standard deviations of the constants are in parentheses, n is

the number of solutes, R is the overall correlation coefficient and $S.D.$ is the overall standard deviation in log L^{16}.

It seems clear that the b constant, 1.22 ± 0.07, is highly significant and therefore that SXPHA is quite acidic. This is not at all consistent with the chemical formulation of SXPHA as a copolymer of (45–55%) methylphenyl- and (45–55%) diphenyl-siloxane that is trimethylsiloxy terminated, and so we repeated measurements on a commercial sample of OV-25 intended for use as a GLC stationary phase; we denote this as SXPHB. The corresponding regression equation for 42 log L values is given as eqn. 3.

Although the b constant in eqn. 3 is much smaller than that in eqn. 2, it is still not zero. Hence either our methodology has produced spurious results or, indeed, our two samples contain hydrogen-bond acidic sites capable of interacting with solute hydrogen-bond bases (and these acidic sites could be part of the actual bulk liquid phase, or they could be sites on the solid support used to pack the columns). We resolved this problem by simply running the IR spectra of the original bulk liquid phases. Fig. 1 shows the spectra obtained between 1600 and 4000 cm^{-1}. Both phases show absorption at round 3500 cm^{-1}, the characteristic OH stretch wavenumber. Absorption is much stronger with sample SXPHA than with SXPHB. This result indicates that both bulk samples contain OH groups, and hence will act as hydrogen-bond acids. The regression equations, above, are hence not artifacts of our methodology but do serve as characteristic equations of the liquid phases. We checked our IR result by treating a packed column of SXPHA with trimethylchlorosilane in order to remove OH. Values of relative retention times, as log t, were regressed as usual to obtain eqn. 4.

This treatment indeed reduces the b constant from 1.22 in eqn. 2 to 0.79 in eqn. 4, as would be expected if the SXPHA column did contain OH groups. We therefore conclude that both our samples, SXPHA and SXPHB, contain OH groups and that our methodology has correctly shown this via the b-constant in eqns. 2–4. As far as our original aim is concerned, the r-constant in eqn. 3 is not particularly large, but the s-constant, 1.23 ± 0.08, must reflect the rather large dipolar/polarisability effect of the aromatic rings and the OH groups. More important, we feel, is our finding that samples of OV-25 may contain previously unsuspected OH groups, that measurably influence sorption at 25°C. and we
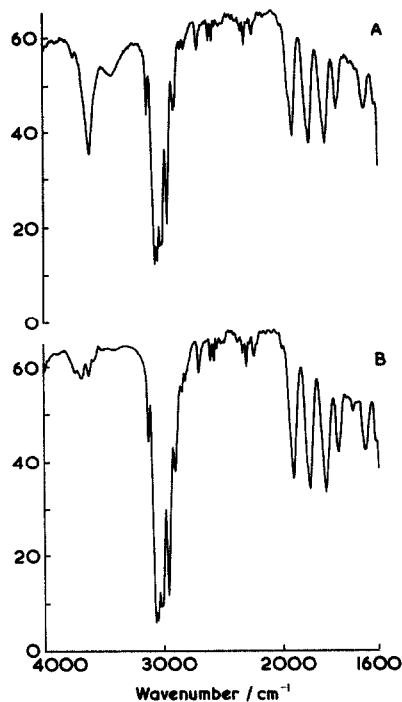

Fig. 1. The IR spectrum of the two samples of (A) SXPHA and (B) SXPHB.

suggest that workers who use the OV or SE series of siloxanes, examine the bulk liquid phases by IR in order to define better the chemical nature of the stationary phases they are using.

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