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Note

Separation of aromatic compounds on phenyl-bonded silica

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Many bonded phases have been synthesised for use in liquid chromatography and a number are available commercially. Of these C_{18} (ODS), C_2, C_6, C_8 and CN-silica are the most widely used. A number of suppliers also offer phenyl bonded phases[1] but these have attracted little attention. The majority of applications have been in the separation of peptides (for example ref. 2) and some work has been carried out on pharmaceuticals such as propanolol[3]. Generally phenyl phases have been regarded as being more polar than ODS-silica.

As part of a study into the use of alkylarylketones as retention index standards[4] and of their application to determining retention constants for stationary phases[5], it was found that the indices of a set of standards varied markedly between alkyl-bonded and phenyl-bonded phases. In particular toluene appeared to be repelled from the stationary phase. As this was contrary to the anticipated affinity of phenyl phases for aryl-hydrocarbons the present study was undertaken to examine the interaction of alkylbenzenes in greater detail.

EXPERIMENTAL

Conditions were as described in ref. 4. Alkylbenzene standards were as described in ref. 7.

RESULTS AND DISCUSSION

In gas–liquid chromatography (GLC), stationary phases incorporating phenyl groups such as OV-17 or SE-52 are frequently chosen for the analysis of aromatic compounds, because they are considered to be more compatible with the samples than dimethyl-silicones such as OV-1 or SE-30. It was therefore expected that similar behaviour might be expected on high-performance liquid chromatography (HPLC), with neutral aromatic compounds being strongly retained on phenyl-bonded silica columns. However, in the recent retention index study the opposite seemed to be found, toluene having a lower retention index on Spherisorb phenyl than on ODS Hypersil[4] (Table I). Thus, compared to the alkylarylketones used as a reference scale, toluene appears to be less soluble in a phenyl-bonded phase than in a hydrocarbon phase. There were also differences in the indices of the other test compounds particu-

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larly of the more polar compounds *p*-cresol and benzyl alcohol which was ascribed to the increased polarity of the phase. Except for phenetole the non-polar compounds showed only small changes.

TABLE I

RETENTION INDICES OF STANDARD COMPOUNDS ON ODS-HYPERSIL AND SPHERISORB PHENYL*

Compound	*Retention index***	
	ODS-Hypersil (methanol–water, 70:30)	*Spherisorb phenyl (methanol–water, 30:70)*
Toluene	1047 (k' = 2.31)	745 (k' = 2.08)
Hexan-2-one	849	711
Benzylalcohol	735	543
2-Phenylethanol	795	625
p-Cresol	818	618
Nitrobenzene	869	802
Methylbenzoate	926	848
Phenetole	1022	809

* From ref. 4, mobile phases selected so that k' of toluene are similar.

** Alkylarylketone scale.

This marked relative change in the retention of arylhydrocarbons had also been noted in a study of nitro-aromatic compounds on phenyl ether-, phenyl- and ODS-bonded phases[6]. On ODS-silica, benzene (capacity factor, k' = 8.18) was eluted after the mono- to trinitrobenzenes, (k' = 6.95–3.13) whereas on phenyl-silica benzene (k' = 1.28) was eluted before the mono- to trinitrobenzenes (k' = 3.48–1.77). On the aryl-ether phase the order of elution was reversed compared to ODS-silica and a charge-transfer interaction was thought to be present between the column and the nitrobenzenes.

In the present study the high eluent polarity needed to retain toluene on the phenyl phase was also unexpected as it was similar to that required for a C_2 (SAS-Hypersil) column[4].

In order to study the interaction further an earlier study of the alkylbenzenes on alkyl-bonded silicas[7] was extended to the phenyl-bonded phase (Table II).

Using methanol–water (30:70) as eluent gave results similar to those obtained previously[4], toluene retention index = 739. The *n*-alkylbenzenes showed a good correlation between carbon number and log k' with a similar slope to the reference scale (Table III). Similar results were obtained for acetonitrile–water (10:90) as eluent except that the retention indices were all higher. They increased further if acetonitrile–water (20:80) was used. These changes in indices were much greater than those found previously for the test compounds when the solvent was changed from 20–80% methanol in water[4]. However in their study using an alkan-2-one scale, Baker and Ma[8] found a marked decrease for andesterone of about 100 units between 10 and 20% acetonitrile in water on μBondapak CN.

Thus, although retention indices are apparently not very sensitive to solvent

TABLE II

CAPACITY FACTORS AND RETENTION INDICES (I) OF ARYLHYDROCARBONS ON A SPHERISORB PHENYL COLUMN USING DIFFERENT SOLVENTS

Compound	*Solvent*					
	Methanol–water (30:70)		*Acetonitrile–water (10:90)*		*Acetonitrile–water (20:80)*	
	k'	I	k'	I	k'	I
Benzene	1.08	634	1.69	668	1.69	776
Toluene	1.69	734	3.23	785	2.85	881
Ethylbenzene	2.69	833	5.92	895	4.77	986
o-Xylene	2.54	821			4.38	967
m-Xylene	2.69	833			4.54	976
p-Xylene	2.69	833			4.38	967
Propylbenzene	4.69	952	12.5	1030	8.54	1103
Isopropylbenzene	4.00	918			7.54	1078
1,2,3-Trimethylbenzene	3.92	914			6.54	1049
1,2,4-Trimethylbenzene	3.92	914			7.00	1064
1,3,5-Trimethylbenzene	4.08	922			7.54	1078
n-Butylbenzene	8.54	1079	28.2	1177	15.6	1225
Isobutylbenzene	7.62	1054			14.1	1205
sec.-Butylbenzene	7.23	1043			13.1	1190
tert.-Butylbenzene	5.92	1001			11.0	1155
1,2,3,4-Tetramethylbenzene	5.85	999			9.92	1134

composition changes, when the solvent polarity changes markedly as it does at the ends of the composition scale, quite large index shifts can be found, particularly if the sample functional group is different to that in the standard.

Although it was hoped that the phenyl phase interactions would lead to a greater discrimination between the alkylbenzenes, the order of elution and the resolutions of isomeric compounds were similar to those obtained previously on alkyl bonded silica[7].

TABLE III

CORRELATION OF LOG k' WITH CARBON NUMBER (C_n) FOR ALKYLARYLKETONE STANDARDS AND n-ALKYLBENZENES ON SPHERISORB PHENYL

Compounds	*Eluents*		
	Methanol–water (30:70)	*Acetonitrile–water (10:90)*	*Acetonitrile–water (20:80)*
Alkylarylketones			
Correlation*	0.9997	0.9993	0.9998
Slope	$2.042 \cdot 10^{-3}$	$2.403 \cdot 10^{-3}$	$2.152 \cdot 10^{-3}$
n-Alkylbenzenes			
Correlation	0.9978	0.9981	0.9994
Slope	$2.24 \cdot 10^{-3}$	$3.033 \cdot 10^{-3}$	$2.409 \cdot 10^{-3}$

* For $\log k' = a\,(C_n \times 100) + b$. Using values from Table II.

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