

Selectivity of carbon packing materials in comparison with octadecylsilyl- and pyrenylethylsilylsilica gels in reversed-phase liquid chromatography^a

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(First received February 5th, 1991; revised manuscript received March 19th, 1991)

ABSTRACT

The retention selectivity of graphitic carbon packing materials was compared with those of octadecylsilyl- and pyrenylethylsilylsilica packing materials in reversed-phase liquid chromatography. A carbon stationary phase showed the highest hydrophobicity and selective retention of planar, unsaturated compounds. The presence of hydrophilic groups did not cause as great a retention decrease on carbon as on silica-based materials. A much greater influence of structural planarity of solutes on selectivity was observed with carbon than with silica-based phases, presumably because the solute planarity emphasizes the interaction with the graphite surface based on charge transfer and dispersion forces. Pyrenylethyl-bonded silica gel was found to be intermediate between alkylsilica and graphitized carbon packing materials with respect to the selectivity based on the electronic and steric interactions with the fused-ring aromatic systems on the stationary phase.

INTRODUCTION

In addition to a variety of silica C₁₈ phases [1,2] and polymer-based packing materials [3,4], several stationary phases capable of charge-transfer-type interactions are currently used for the separation of compounds with structural similarity in reversed-phase liquid chromatography (RPLC) [5–19].

The differences in steric selectivity between polymeric- and monomeric-type silica C₁₈ packing materials have been well documented [20,21]. The selective retention of rigid, compact solutes by polymer-based packing materials has been explained by the contribution of biporous structures of polymer gels [3,4,22], macroporous gels composed of microporous materials. To add positive interactions to the retention process with hydrophobic stationary phases in RPLC, pyrenylethylsilylated (PYE) silica gel was prepared to have charge-transfer, dipole- π and steric interactions. The

^a Presented at the *14th International Symposium on Column Liquid Chromatography, Boston, MA, May 1990*. The majority of the papers presented at this symposium have been published in *J. Chromatogr.*, Vol. 535 (1990) and 536 (1991).

PYE phase provided isomer separations of tetrachlorodibenzo-*p*-dioxins and di-substituted cyclohexanes that were not possible with silica C₁₈ phases [5–10].

Graphitized carbon packing material is one of the extremes of stationary phases for RPLC, possessing rigid, planar surfaces in addition to functions capable of strong charge-transfer interactions [11–19]. These stationary phases have been reported to be useful for the separation of solutes with closely related structures including stereoisomers. Recently, applications of this packing material to isomer separations and mechanistic studies have been reported. In these reports, interactions including steric interaction, charge-transfer and dispersion forces were shown to be responsible for the discrimination of solutes, as studied with unsaturated compounds. The effects of organic solvents and additives have also been studied.

The pyrenyl groups on the PYE phase possesses fused aromatic systems with sixteen π -electrons which may be regarded as a small part of a graphite surface. The PYE phase provided a much greater effect of a planar aromatic structure on retention selectivity than a phenylethylsilylated silica phase [5,8].

A comparison of carbon packing materials with PYE and C₁₈ silica was thought to be of value for providing information on the retention mechanisms with packing materials having large differences in structure. We report here a study of the retention characteristics of graphitized carbon packing materials from two manufacturers in comparison with C₁₈ and pyrene-bonded silica gels. The study indicates that some of the characteristic selectivity of a carbon phase, very different from those of silica C₁₈ phases, occurs with a PYE phase having some structural similarity.

EXPERIMENTAL

The HPLC system consisted of a Model 880-PU pump, a Model 875-UV detector, a Model 830-RI refractive index detector (all from JASCO, Tokyo, Japan) and a C-R4A data processor (Shimadzu, Kyoto, Japan). Chromatographic measurements were carried out at 30°C.

Silica-based packing materials were prepared from Develosil (particle size 5 μm , pore size 11 nm) (Nomura Chemical, Seto, Japan), as reported previously [5,23], and packed into stainless-steel columns [100 mm \times 4.6 mm I.D. for C₁₈ and nitrophenylethyl (NPE) and 150 mm \times 4.6 mm I.D. for pyrenylethyl (PYE)]. Packed carbon columns of Hypercarb, designated carbon I in this paper (Shandon, Runcorn, Cheshire, UK) (100 mm \times 4.7 mm I.D.), Carbonex, designated carbon II (Tonen, Tokyo, Japan) (100 mm \times 4.6 mm I.D.) and a polymer gel column of Shodex DE-613 (Showa Denko, Tokyo, Japan) were loaned by Senshu Kagaku (Tokyo, Japan), Tonen and Showa Denko, respectively. Mobile phases were made up by volume from HPLC-grade solvents.

Electron microscopy was carried out at Nitto Technical Information Centre (Osaka, Japan), as described previously [24], by employing ultra-thin sections of the porous particles embedded in epoxy resin.

RESULTS AND DISCUSSION

Hydrophobic properties

The hydrophobic properties of the packing materials were studied by mea-

suring the retention increase caused by the addition of one methylene group to the solute structure. Table I summarizes the $\alpha(\text{CH}_2)$ values calculated from a values in the equation

$$\log k' = a C_n + b \quad (1)$$

or the slope of the plots of $\log k'$ (capacity factor) against carbon number (C_n) of alkyl groups in alkyl alcohols and alkylbenzenes in aqueous methanol.

Smaller a values were found with PYE than with C_{18} phase, indicating a less hydrophobic character of the PYE phase. The major driving force of hydrophobic interaction is the release of water molecules from the solvation shell around the so-called hydrophobic molecules, by transferring the solute from the aqueous phase to the organic phase in liquid-liquid two-phase systems. From the same mobile phase, the transfer of a methylene group to a C_{18} phase is more favourable than that to a PYE phase, presumably because some solvent-like behaviour can be expected with the aggregated alkyl chains on the C_{18} phase.

However, it has been reported that the a value on a C_{18} phase, or the increase in k' values is slightly smaller than those in partition coefficients in water-organic liquid-liquid two-phase systems [25]. This is due to the restriction of alkyl chains bonded to the silica surface, having a lower density and less mobility than liquid alkanes [1]. The a values with C_1 and C_8 phases, where a solvent-like interaction with the solute is unfavourable owing to the small size of the alkyl groups, are much smaller than those on C_{18} phases [5].

Table I indicates that the a value, or the hydrophobic property of the stationary phase, on the carbon phase is always greater than those on alkyl- or aryl-bonded silica phases. The free-energy change associated with the transfer of one methylene group from water to the stationary phase was about -900 cal/mol with the carbon phase compared with -810 cal/mol on the C_{18} phase. The latter was slightly larger than that previously obtained with a C_{18} phase with a lower surface coverage [25]. The difference between the C_{18} and carbon phases was even greater at a higher methanol concentration. The free energy change associated with the transfer of one methylene

TABLE I
HYDROPHOBIC PROPERTIES OF PACKING MATERIALS

The $\alpha(\text{CH}_2)$ values (retention increment with one additional methylene group in solute structure) calculated from a in eqn. 1 at methanol concentrations from 0 to 80% in the mobile phase. $\alpha(\text{CH}_2) = 10^a$.

Stationary phase	$\alpha(\text{CH}_2)^a$				
	0%	10%	30%	50%	80%
C_{18}	3.84	3.62	2.94	2.25	1.54
PYE	3.27	3.15	2.81	2.13	1.45
Carbon I	4.50	4.09	3.67	2.83	2.10
Carbon II	4.53	4.49	3.74	2.87	2.11

^a Calculated from the retention times of alkyl alcohols ($C_n\text{H}_{2n+1}\text{OH}$, $n=2-5$), except in 80% methanol, where alkylbenzenes (ethylbenzene to amylbenzene) were used.

group from water to the organic phase was -820 to -850 cal/mol for polar solutes and -884 cal/mol for alkane-water partition [26].

The present results are striking if it is assumed that the solutes are partitioned onto the rigid planar graphite surface. Some solvent-like flexibility of a C_{18} stationary phase is expected to give such an interaction to reduce the contact between the C-H surface of a solute and water as in aqueous-organic liquid-liquid partition systems that lowers the free energy of the system. On the other hand, the rigid carbon surface would not be able to completely surround the alkyl chain of the solute.

The results suggest the presence of some positive interactions between the stationary phase and the solute, namely dispersion forces, as suggested by previous workers [21,27]. Karger *et al.* [28] suggested the contribution of dispersion forces on the graphite surface which arises from the high polarizability of the graphite surface, coupled with a high dispersive solubility parameter for a methylene group. Close proximity of the molecular surface of the solute and the stationary phase allowed by mutual steric compatibility should be a critical factor for this to occur.

Polar group selectivity

In order to show the nature of the interaction between polar functional groups and the stationary phase, the $\log k'$ values of monosubstituted alkanes (RX) on carbon and C_{18} phases were plotted against the carbon number of solutes, as shown in Fig. 1. Straight lines of good linearity were obtained for each homologous series of compounds. The plots were fitted to eqn. 1, and the resulting slopes (a values) and intercepts (b values) are listed in Table II.

The slopes (a values) obtained on one stationary phase were close to each other regardless of the functional groups of the solutes. The a values indicate how hydrophobic the stationary phase is, whereas the intercept (b values) gives information on how favourable the specific interaction is between the functional group and the stationary phase. Any difference in behaviour should be related to the stationary phase effect, because the interaction with mobile phase solvents is cancelled by employing the same mobile phase for all the columns.

On silica C_{18} , hydrophilic groups such as OH or CHO caused a large decrease

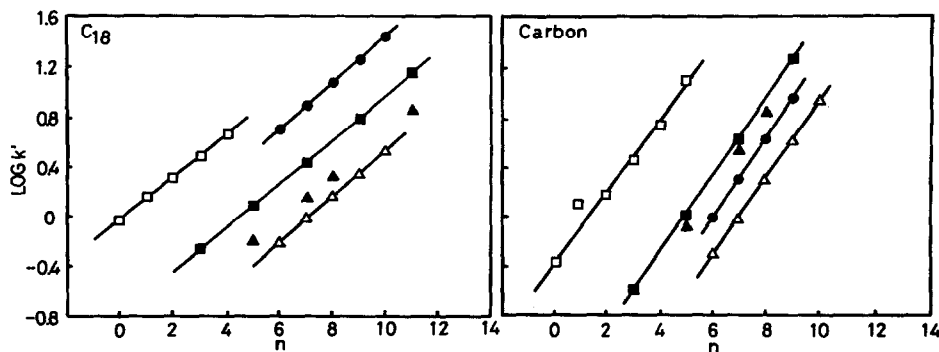


Fig. 1. Plots of $\log k'$ values against the carbon number of alkyl groups of monosubstituted alkanes on (right) carbon and (left) C_{18} phases with methanol-water (80:20). $\square = C_6H_5C_nH_{2n+1}$; $\blacksquare = C_nH_{2n+1}COOCH_3$; $\bullet = C_nH_{2n+2}$; $\triangle = C_nH_{2n+1}OH$; $\blacktriangle = C_nH_{2n+1}CHO$.

TABLE II
EFFECT OF TERMINAL GROUPS ON RETENTION

Stationary phase	<i>b</i> value (<i>a</i> value) ^a						
	C ₆ H ₅	H	COOCH ₃	CHO	OH	COOH	NH ₂
C ₁₈ ^b	-0.03 (0.17)	-0.39 (0.18)	-0.80 (0.18)	-1.09 (0.18)	-1.33 (0.19)		
PYE ^b	-0.36 (0.15)	-0.84 (0.14)	-0.71 (0.13)	-1.19 (0.15)	-1.45 (0.16)		
Carbon I ^b	-0.38 (0.29)	-1.96 (0.32)	-1.52 (0.31)	-1.62 (0.31)	-2.28 (0.32)		
Carbon I (pH 2.5) ^c					-2.12 (0.45)	-1.52 (0.43)	-3.46 (0.44)
Carbon I (pH 12) ^d					-2.11 (0.45)	-2.11 (0.41)	-1.95 (0.44)

^a Calculated according to the equation $\log k' = a C_n + b$, where C_n is the number of carbon atoms in the alkyl group in each homologous series of compounds.

^b 80% methanol.

^c 50% methanol, 0.02 M H₃PO₄-NaH₂PO₄.

^d 50% methanol, 0.02 M NaOH-Na₂HPO₄.

in *b* values, and a large increase in *b* was seen with the phenyl group, taking the alkanes (X = H) as standard. Although the PYE showed a similar tendency, the decrease in *b* values was noticeably smaller for CHO or COOCH₃ groups. This can be explained in terms of the dipole- π interactions with the stationary phase.

The tendency on the carbon phase was different. Hydrophilic groups, especially those containing a carbonyl group, were actually more favoured than H. The retention decrease due to the presence of an OH group was found to be very small in spite of the greater hydrophobic selectivity of this stationary phase. The increased interaction of a hydroxyl group with the mobile phase seems to be counteracted by an increased interaction with the stationary phase.

The results can be explained on the basis of proton donor- π or electron donor-acceptor interactions. Complexation of proton donors with phenyl rings has been reported using NMR and UV spectroscopy [29,30]. Bassler *et al.* [15] showed the correlation between the pK_a values of aromatic compounds and the retention on a carbon phase working as an electron acceptor in the normal-phase mode.

The carbon phase gave high *a* values, generally resulting in a greater difference in retention than the other phases based on the increase in molecular weight. Logically, the carbon phase generally gave much greater separation factors than silica-based materials in the same mobile phase for a homologous series of compounds.

Stronger eluents should be used with a carbon phase to avoid prolonged retention times. Fig. 2 illustrates the characteristics shown above in the chromatogram of alkylamines in an aqueous mobile phase at high pH, where silica-based columns and polymer-based columns are either useless or accompanied by tailing. The excellent chemical stability of carbon phases under extreme pH values is an obvious advantage.

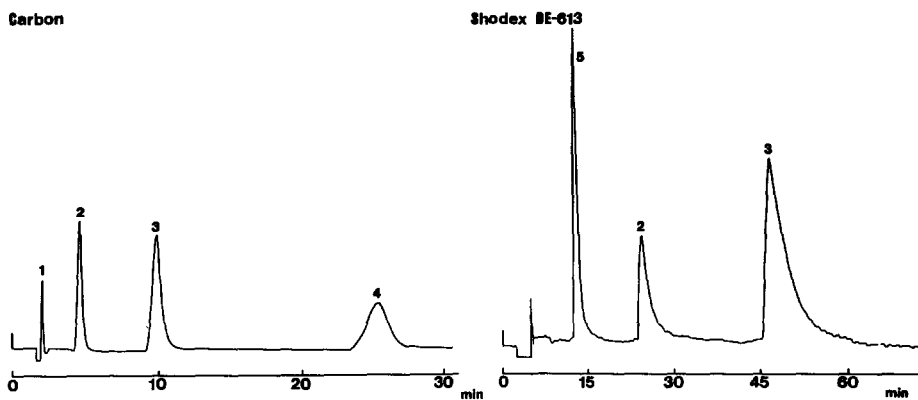


Fig. 2. Separation of alkylamines on carbon- and polymer-based packing materials. Mobile phase: Shodex DE-613 (polymer-based): 20% acetonitrile in 0.013 *M* phosphate buffer (pH 11.7). Carbon: 30% acetonitrile in 0.02 *M* phosphate buffer (pH 12.1). Solutes: 1 = butylamine; 2 = hexylamine; 3 = heptylamine; 4 = octylamine; 5 = cyclohexylamine.

Charge-transfer interaction

In Fig. 3, $\log k'$ values of monosubstituted benzenes on carbon I and silica-based phases are plotted against $\log P$ values [31] obtained from 1-octanol–water partition. A straight line was drawn through the plots for benzene, toluene and ethylbenzene. The contribution of hydrophobic interaction is clearly seen on every phase from the contribution of alkyl groups to the retention.

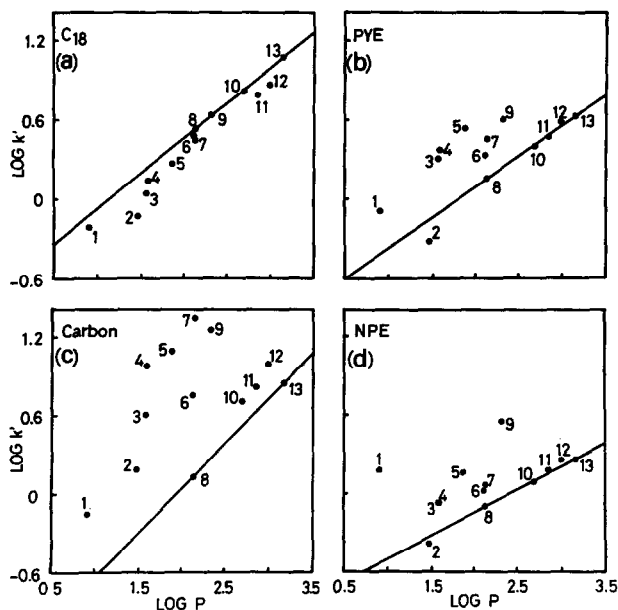


Fig. 3. Plots of $\log k'$ values against $\log P$ values of monosubstituted benzenes in 60% methanol. (a) C_{18} ; (b) PYE; (c) carbon; (d) NPE. Substituents: 1 = NH_2 ; 2 = OH ; 3 = CN ; 4 = $COCH_3$; 5 = NO_2 ; 6 = OCH_3 ; 7 = $COOCH_3$; 8 = H ; 9 = $N(CH_3)_2$; 10 = CH_3 ; 11 = Cl ; 12 = Br ; 13 = C_2H_5 .

Fairly good linearity was observed with silica C_{18} phase, as reported previously [32], indicating that the hydrophobic interaction plays a major role in determining the retention on this stationary phase, while additional factors provided by the stationary phase resulted in scattered plots on PYE, NPE and carbon phases.

All the points in Fig. 3c were above the straight line connecting the plots for benzene and ethylbenzene. The results indicate that any substituents, electron-withdrawing or electron-donating, with increase in molecular weight can contribute to the increase in k' on the carbon phase relative to aqueous-organic liquid-liquid partition or the chromatographic system with the C_{18} phase.

The results on the carbon phase, indicating the preferential retention of compounds with higher molecular weight, particularly for those with electron-withdrawing substituents (Nos. 4, 5 and 7 in Fig. 3), agree with a retention mechanism including the contributions of the dispersion forces and the charge-transfer interactions in addition to the hydrophobic interaction. The correlation between the magnitude of dispersion forces and molecular volume has been documented [33]. The results clearly show the utility of the carbon phase for the separation of compounds with similar hydrophobicities which were difficult to separate with the C_{18} phase (e.g. Nos. 6, 7 and 8 in Fig. 3).

In contrast to the carbon phase, the NPE phase showed a clear preference for compounds with electron-donating substituents, as expected on the basis of charge-transfer interactions between the solutes and the stationary phase. The results in Fig. 3 suggest that the PYE phase possesses some similarity to the carbon phase with respect to the selectivity for solutes with polar functional groups.

Steric selectivity

Chemically bonded silica stationary phases prepared from silanes of different functionality [20,21,34] or different alkyl chain length [35] showed the different selectivities for the aromatic compounds of different planarity. The rigid planar structure of the PYE phase was shown to be responsible for the better separation of disubstituted cyclohexanes than on C_{18} [8]. The use of cycloalkanes is appropriate for investigating the steric selectivity of various types of stationary phases, because only dispersion forces are expected to play a role in the interaction with the stationary phase.

As shown in Table III, the separation factor, $\alpha = k'_{(\text{decalin})}/k'_{(\text{adamantane})}$, was very large on the carbon phase compared with silica-based materials. The PYE phase showed a slightly greater steric selectivity than C_{18} . Note here that the results also include the difference in the hydrophobic properties between the two phases. The more hydrophobic C_{18} should have given a much larger α value than PYE if the recognition is achieved only on the basis of the hydrophobic effect. The slightly greater separation factor between decalin and adamantane on PYE is an indication of the selective retention of decalin, the more planar of the two. A clear difference in steric selectivity was seen between C_{18} and PYE when aromatic compounds, triphenylene and *o*-terphenyl, were used as probes [5,34].

The carbon phase resulted in much larger α values for alkanes with different bulkiness, indicating the retention of bulky, non-planar compounds to be unfavourable on this phase. It is interesting that a larger $k'_{(\text{hexane})}/k'_{(\text{cyclohexane})}$ ratio was found on carbon than C_{18} . This is in contrast to the polymer-based phases [4,22], which

TABLE III
 STERIC SELECTIVITY FOR CYCLOALKANES

Mobile phase: methanol-water (80:20).

Stationary phase	k'		α^a	k'		α^b
	Hexane	Cyclohexane		Adamantane	<i>trans</i> -Decalin	
C ₁₈	5.24	3.73	1.40	10.3	15.9	1.54
PYE	0.99	0.82	1.21	2.24	3.47	1.55
Carbon I	0.97	0.32	3.0	0.79	3.55	4.49
Carbon II	0.52	0.17	3.0	0.45	2.20	4.86
NPE	—	—	—	0.83	0.98	1.19

^a Separation factor, $k'_{\text{hexane}}/k'_{\text{cyclohexane}}$.

^b Separation factor, $k'_{\text{trans-decalin}}/k'_{\text{adamantane}}$.

showed selective retention of the more rigid, compact solutes, with the order of preference planar aromatic compounds, bulky aromatic compounds, cycloaliphatic compounds, followed by the straight-chain alkyl compounds. The three-dimensional network structures of polymer gels seemed to be responsible for the selectivity [3,4,22].

The steric selectivity of the carbon phase is different from those of either polymer- or silica-based materials, showing preference in the order planar aromatic, bulky aromatic, *n*-alkyl and cycloaliphatic compounds, with adamantane showing a very small retention. The results indicate the contribution of dispersion forces to retention, because the greatest dispersion interaction is expected with planar solutes. Cyclohexane cannot assume a planar structure with the carbon chain like hexane. A cyclohex-

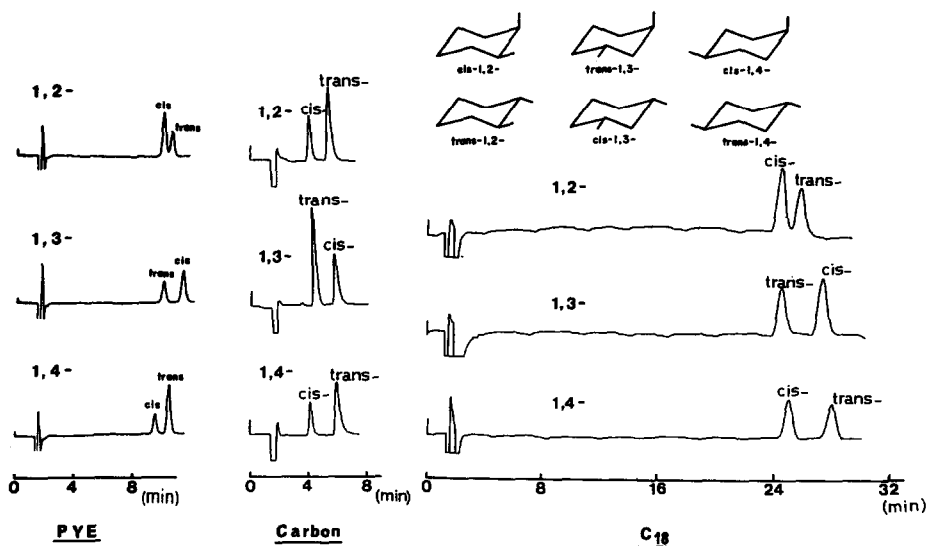


Fig. 4. Separation of dimethylcyclohexanes on C₁₈, PYE and carbon packing materials. Mobile phase: 70% methanol.

TABLE IV
SELECTIVITY FOR DISUBSTITUTED CYCLOHEXANES

Mobile phase: methanol–water (70:30).

Disubstituted cyclohexane solute ^a	Separation factor, α , between <i>cis</i> - and <i>trans</i> -isomers (k') ^b			
	C ₁₈	PYE	Carbon I	Carbon II
1,2-(CH ₃) ₂	1.05(<i>c</i> ;23.7)	1.07(<i>c</i> ;4.39)	1.51(<i>c</i> ;2.11)	1.45(<i>c</i> ;1.49)
1,3-(CH ₃) ₂	1.12(<i>t</i> ;23.8)	1.16(<i>t</i> ;4.38)	1.49(<i>t</i> ;2.44)	1.58(<i>t</i> ;1.67)
1,4-(CH ₃) ₂	1.13(<i>c</i> ;23.7)	1.13(<i>c</i> ;4.21)	1.67(<i>c</i> ;2.22)	1.58(<i>c</i> ;1.57)
Menthol/isomenthol	1.10(4.63)	1.20(2.01)	1.71(3.11)	1.79(1.79)
1,2-(COOEt) ₂	1.01(<i>t</i> ;2.79)	1.19(<i>t</i> ;3.41)	1.11(<i>c</i> ;3.43)	1.03(<i>c</i> ;2.08)
1,2-(COOPr- <i>n</i>) ₂	1.01(<i>t</i> ;6.98)	1.19(<i>t</i> ;6.81)	1.32(<i>c</i> ;10.3)	1.1(<i>c</i> ;6.7) ^c
1,2-(COOBu- <i>n</i>) ₂	1.01(<i>c</i> ;17.7)	1.18(<i>t</i> ;15.6)	1.16(<i>c</i> ;4.33) ^d	—
1,2-(COOBu- <i>t</i>) ₂	1.08(<i>t</i> ;13.3)	1.20(<i>t</i> ;8.27)	1.56(<i>c</i> ;0.56) ^d	—
1,4-(COOEt) ₂	1.10(<i>c</i> ;2.40)	1.06(<i>c</i> ;3.82)	4.88(<i>c</i> ;1.81)	4.83(<i>c</i> ;1.12)
1,4-(COOBu- <i>n</i>) ₂	1.28(<i>c</i> ;15.5)	1.14(<i>c</i> ;18.0)	5.87(<i>c</i> ;2.49) ^d	—
1,4-(COOBu- <i>t</i>) ₂	1.25(<i>c</i> ;11.5)	1.16(<i>c</i> ;8.92)	2.84(<i>c</i> ;0.83) ^c	—
1,2-(OH) ₂ ^e	1.07(<i>t</i> ;6.62)	1.09(<i>t</i> ;4.20)	1.10(<i>t</i> ;2.37)	—
1,3-(OH) ₂ ^e	1.03(<i>c</i> ;2.32)	1.14(<i>t</i> ;1.67)	1.25(<i>t</i> ;1.76)	—
1,4-(OH) ₂ ^e	5.42(<i>t</i> ;0.46)	3.39(<i>t</i> ;0.61)	1.05(<i>t</i> ;1.70)	—

^a ET = ethyl; Pr-*n* = *n*-propyl; Bu-*n* = *n*-butyl; Bu-*t* = *tert.*-butyl.

^b k' of the first peak indicated by *t* or *c*, representing *trans*- or *cis*-isomer, respectively, in parentheses.

^c Tailed peaks.

^d Mobile phase: methanol–water (90:10).

^e Mobile phase: methanol–water (5:95).

ane-bonded silica phase actually disfavoured planar aromatic compounds [5]. Previous workers have discussed the retention tendency of xylenes based on the points of contact [11,14] with the carbon surface. The present results with cycloalkanes, which are electronically most inert, support their conclusion.

Selectivity for disubstituted cyclohexanes

In the separation of dimethylcyclohexanes, those with two equatorial methyl groups, *trans*-1,2-, *cis*-1,3- and *trans*-1,4-isomers, were preferentially retained by all the stationary phases. As shown in Fig. 4 and Table IV, the PYE phase resulted in a similar resolution in a much shorter time than C₁₈. This tendency was further emphasized on the carbon phase, which showed a much greater preference toward the more planar isomers, resulting in an easy separation between the *trans* and *cis* forms of dimethylcyclohexanes.

In the case of cyclohexanediols, those with two equatorial hydroxyl groups, *trans*-1,2- and *trans*-1,4-diols, generally resulted in a shorter retention owing to the easier solvation in the mobile phase than those possessing an axial hydroxyl group. The C₁₈ phase gave an easy separation of 1,4-diols, but could not separate 1,3-diols owing to the contribution of internal hydrogen bonding in the *cis* isomer [8]. The PYE phase provided a better separation for isomers of 1,2- and 1,3-diols than the C₁₈ phase. The carbon phase resulted in a much easier separation of 1,3-diol isomers, but gave a very small separation factor for 1,4-diol isomers. This is due to the preference toward the more planar compounds shown by the carbon phase.

TABLE V

COMPARISON OF SELECTIVITIES TOWARD SIMPLE ALKENES

Mobile phase: methanol-water (70:30).

Solute	$\alpha(k')$ ^a		
	C ₁₈	PYE	Carbon I
1-Heptene	— (13.9)	— (2.98)	— (2.87)
2-Heptene	1.09 (Z;13.0)	1.08 (Z;2.69)	1.27 (Z;2.25)
3-Heptene	1.07 (Z;12.8)	1.04 (Z;2.62)	1.23 (Z;1.88)
1-Octene	— (23.7)	— (4.64)	— (6.55)
2-Octene	1.11 (Z;22.1)	1.07 (Z;4.17)	1.41 (Z;4.95)

^a Separation factor, α , between *E* and *Z* forms, and the configuration and k' of the first peak in parentheses.

The C₁₈ phase gave little separation of isomers of 1,2-cyclohexanedicarboxylic acid dialkyl esters, whereas the PYE phase provided a much better separation based on the favourable dipole- π interaction with *cis*-1,2-diester having the two substituents in axial-equatorial positions [8]. The carbon phase also provided an easy separation. Preference, however, was shown toward the isomers with two equatorial ester groups. Here the dipole- π interaction seemed to be overwhelmed by the preference for planar solutes.

Overall, the results with cyclohexane derivatives indicate the strong contribution of the steric effect on the carbon phase in addition to the hydrophobic interactions. One can obtain much better separations in a much shorter time by employing

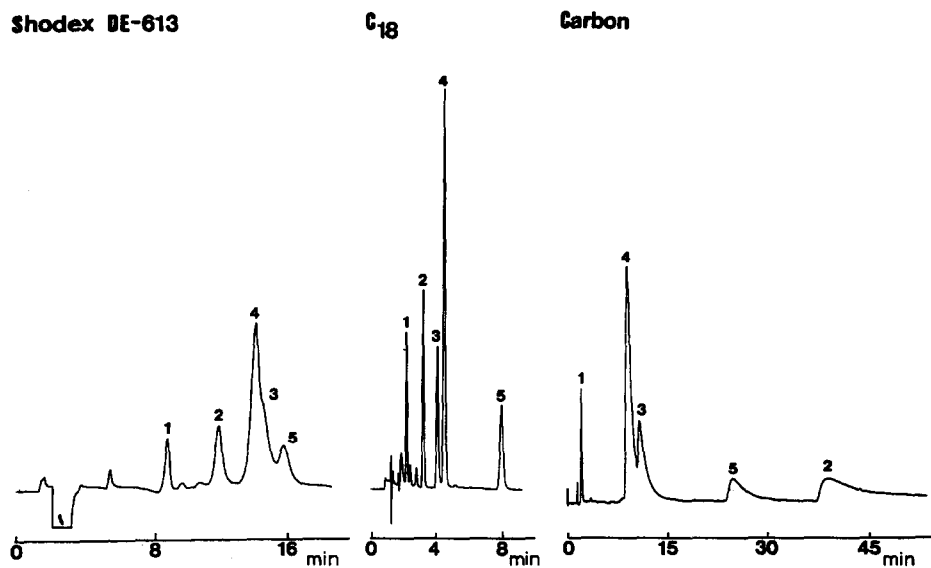


Fig. 5. Difference in selectivity toward aromatic hydrocarbons. (a) Polymer-based (in 50% tetrahydrofuran); (b) C₁₈ (in 80% methanol); (c) carbon (in 80% methanol). Solute: (1) benzene; 2 = naphthalene; (3) triptycene; (4) diphenylmethane; (5) triphenylmethane.

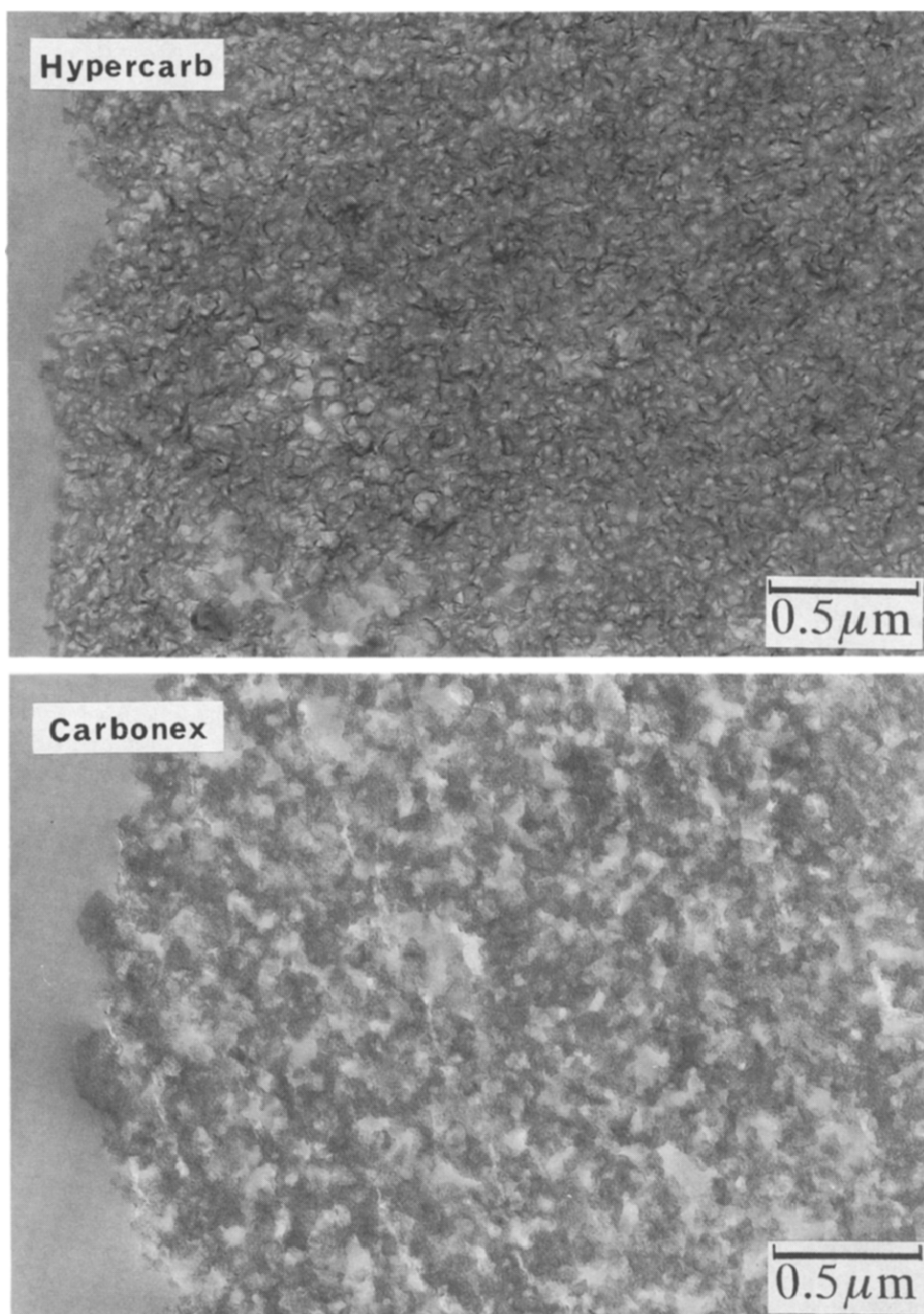


Fig. 6. Transmission electron micrographs of carbon packing material. (top) Hypercarb (carbon I); (bottom) Carbonex (carbon II).

an appropriate column. Although little tailing was seen with the carbon phase, the PYE phase showed a good performance with a selectivity similar to that of carbon in many instances.

Olefins

A comparison of selectivity toward simple alkenes is shown in Table V, which indicates the utility of the carbon phase in the separation of olefin isomers. The carbon phase gave much greater separation factors for the isomers, with preference toward terminal olefins over internal olefins and *E* isomers over *Z* isomers. The former observation can be explained by the greater exposure of π -electrons of the terminal olefins as in argentation chromatography [36], and the latter by structural planarity.

Fig. 5 shows an example of the different steric selectivities of a carbon phase from those of silica C_{18} and polymer-based packing materials for aromatic compounds. The number of π -electrons aligned on a plane has a critical influence on the selectivity on the carbon phase.

Comparison between the two carbon packing materials

Transmission electron micrographs of carbon packing materials I and II are shown in Fig. 6. The sizes of the primary structures of the latter are relatively uniform, within 50–80 nm, whereas the former possesses primary structures within the range 30–40 nm with some very large pores and skeletons. The chromatographic properties of these materials were very similar to each other with respect to selectivity for hydrocarbons, as shown in Tables I, III and IV, in spite of the difference in the internal structures and in the method of preparation. Carbon I was prepared from phenol–formaldehyde polymers via a template method [11], whereas carbon II was prepared from petroleum pitch without using a template.

CONCLUSIONS

Graphitic carbon packing materials showed retention characteristics based on the steric, charge-transfer and dispersion interactions of the solutes with the graphite surface, regardless of the method of preparation of the particles. These interactions on a carbon phase are much greater than those on any silica-based packing materials, resulting in the preferential retention of planar compounds. The silica-based PYE phase showed properties intermediate between those of the carbon and alkyl-type silica-based stationary phases.

ACKNOWLEDGEMENT

The authors are grateful to Tonen, Senshu Kagaku and Showa Denko for the loan of the carbon and polymer gel columns.

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