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NEW TYPE OF CARBONACEOUS ADSORBENT FOR HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

A new type of carbonaceous adsorbent, prepared by a replicate method on a silica gel matrix, was examined under the high-performance liquid chromatographic conditions. The measurements were performed with organic substances of various chemical structures (ketones, aromatic derivatives) and with mobile phases of various polarities. Some conclusions have been drawn on the properties of the adsorbent, on the basis of the dependence of t'_R or $\ln k$ on the number of solute carbon atoms and on the molecular refraction.

INTRODUCTION

Interest in carbonaceous adsorbents as stationary phases in high-performance liquid chromatography (HPLC) has recently increased because of the (theoretical) non-polar character of these materials and the possibility of using them over a wide pH range. The principal problem is the preparation of a suitable type of carbon that would meet the HPLC requirements, namely, mechanical strength of the particles, homogeneity and a suitable specific surface area.

The first attempt to prepare a carbonaceous sorbent suitable for HPLC was made by Guiochon and co-workers¹⁻³ who agglomerated carbon black by pyrolytic decomposition of benzene followed by graphitization. This procedure was subsequently modified⁴⁻⁶ and the surface of silica gel was coated by carbon obtained by pyrolytic decomposition of benzene. Another approach is based on the electrochemical reduction of poly(tetrafluoroethylene) with lithium amalgam at room temperature⁷⁻¹². The excellent selectivity in gas chromatography of commercial graphitized carbon black, Carbo-pack B, was also utilized in HPLC by Ciccioi *et al.*¹³.

The newest carbonaceous sorbent is PGC (porous glassy carbon)¹⁴, whose properties best satisfy the HPLC requirements. Active carbon CF-32-1, used in the present study, belongs in the same category. Recently, the field of carbonaceous sorbents in HPLC was reviewed critically by Knox *et al.*¹⁵.

We now report the chromatographic behaviour of a new type of carbon support, Carbon CF-32-1.

EXPERIMENTAL

All the measurements were carried out with carbon CF-32-1 prepared in the Institute of Polymers of the Slovak Academy of Sciences in Bratislava, by using a replicate method —the pyrolysis of a phenol formaldehyde resin on a silica gel matrix¹⁶. It has been found by x-ray diffraction analysis that this material has a partially crystalline structure. A photograph of carbon CF-32-1, obtained on a scanning electron microscope, is given in Fig. 1. The average carbon particle size is 62 nm, the specific surface area $432 \text{ m}^2 \text{ g}^{-1}$ and the bulk weight 0.425 g cm^{-3} .

Pure methanol, a mixture of methanol and butanol, a 10% solution of butanol in methanol containing 10^{-5} M naphthalene or *p,p'*-tetraphenyl, dichloromethane and a mixture of dichloromethane and *n*-heptane were used as the mobile phases.

The measurements were performed on a Pye Unicam LC-XP liquid chro-

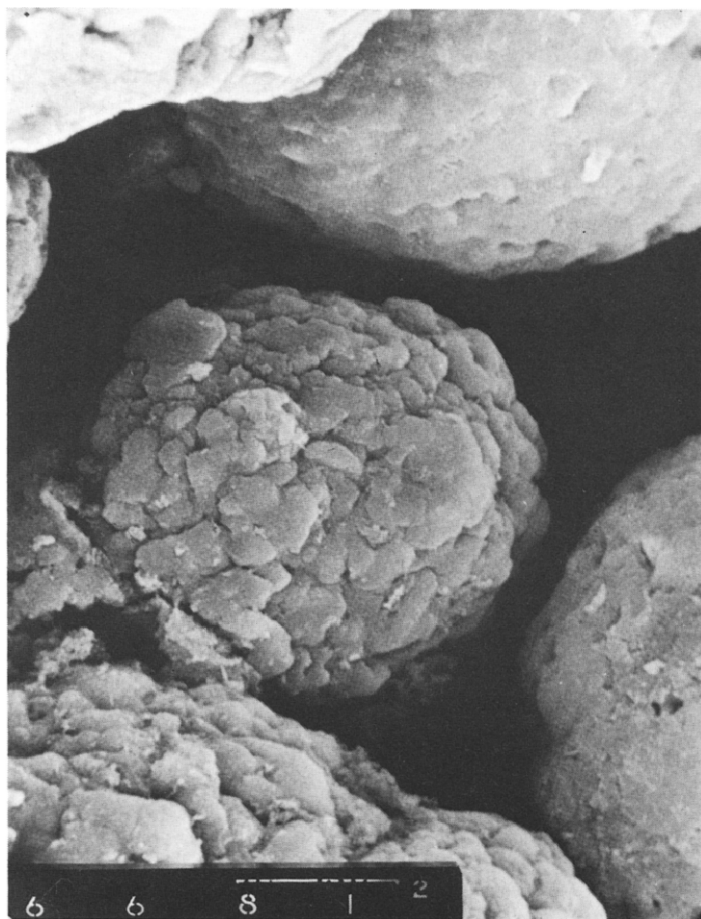


Fig. 1. Scanning electron microphotograph of carbon CF-32-1. Magnification: 3000.

matograph with a variable wavelength UV photometric detector and an LC-XPD pump. A glass column (150 × 3.2 mm I.D.) was packed with the sorbent using the suspension method. The samples (0.1–1.0 μl) were injected with a Hamilton micro-syringe.

RESULTS AND DISCUSSION

As expected, the carbonaceous packing is suitable for separations of homologous series of compounds, which depend on the hydrophobic selectivity.

Methanol was used as the mobile phase in the preliminary experiments. However, as a small highly polar molecule (thus with a low elution strength on non-polar carbon) this solvent cannot elute non-polar substances or substances with low polarities. Therefore, *n*-butanol was added to increase the elution strength. The dependence of the logarithm of the capacity factor, $\ln k$, on the number of carbon atoms in an homologous series of 2-*n*-alkanones is given in Fig. 2. Compared with pure methanol as solvent, the retention times decreased, especially those of the higher ketones. With increasing content of *n*-butanol the differences in retention decrease, as do the slopes of the linear dependences. This is caused by a decrease in the effect of the carbonyl group in the molecules, and the length of the alkyl chain plays a greater role with higher homologues. 2-Heptanone and higher ketones, as well as aromatic substances, were not eluted with pure methanol and their peaks were considerably broadened in the mixed solvent.

To improve the peak symmetry, naphthalene or *p,p'*-tetraphenyl was added to a 10% solution of *n*-butanol in methanol. The peak symmetry of aromatic hydrocarbons improved considerably, but no effect was observed with polar ketones.

The elution patterns of the studied substances changed greatly when dichloro-

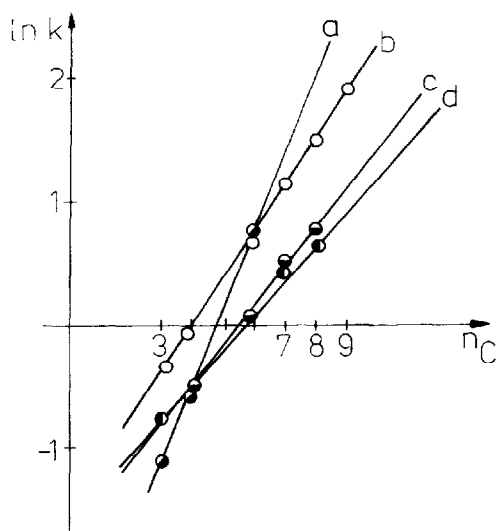


Fig. 2. Dependence of $\ln k$ on the number of carbon atoms (n_C) of *n*-alkanones in pure methanol (a), 5% butanol in methanol (b), 10% butanol in methanol (c) and 20% butanol in methanol (d).

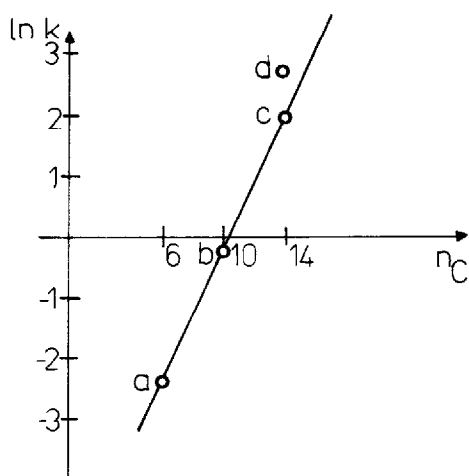


Fig. 3. Dependence of $\ln k$ on the number of carbon atoms of aromatic carbocyclic hydrocarbons. a, benzene; b, naphthalene; c, phenanthrene; d, anthracene.

methane was used as the mobile phase. While ketones were practically unresolved, aromatic compounds were eluted and separated.

Although charge-transfer (π complexes) and polarization interactions play a rôle in solute-sorbent interactions, the largest contribution to adsorption on the carbon surface is associated with dispersion forces (and thus the geometric structure) of the sorbate molecules. The linear dependences of $\ln k$ on the number of carbon atoms in homologous series of aromatic compounds, Figs 3 and 4, illustrate the separation possibilities. For example, it is possible to separate benzene, naphthalene and phenanthrene which is more aromatic than anthracene.

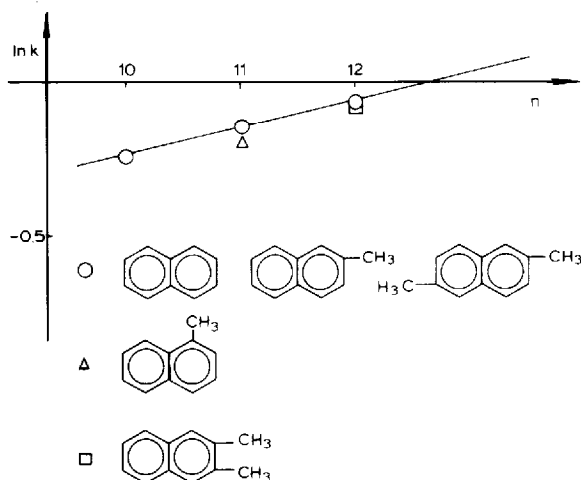


Fig. 4. Dependence of $\ln k$ on the number of carbon atoms of naphthalene and its methyl and dimethyl derivatives.

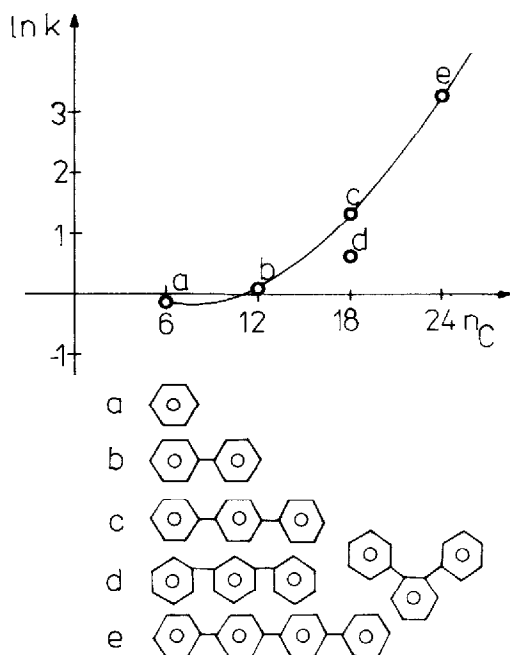


Fig. 5. Dependence of $\ln k$ on the number of carbon atoms in the pseudohomologous series of benzene, biphenyl, triphenyls and *p,p'*-tetraphenyl.

The effect of substitution with methyl groups was studied for naphthalene derivatives. As shown in Fig. 4, there is a linear dependence of $\ln k$ on the number of carbon atoms in the series naphthalene, 2-methylnaphthalene, 2,3- and 2,6-dimethylnaphthalene. The deviation found for 1-methylnaphthalene is caused by steric effects.

The effect of the structure of the chromatographed substances is evidenced by the plot of $\ln k$ vs. the number of carbon atoms for the pseudohomologous series, benzene, biphenyl, *p*-triphenyl and *p,p'*-tetraphenyl (Fig. 5). The non-linearity of this dependence stems from the differences in the geometric structures of the molecules. For example, benzene is a planar molecule that is in overall close contact with the carbonaceous adsorbent; however, biphenyl is a non-planar molecule, formed by benzene rings at an angle of 40° . Thus biphenyl is much less strongly retained than

TABLE I

CORRECTED RETENTION TIMES (t'_R) IN DICHLOROMETHANE

Compound	t'_R (min)
Biphenyl	1.09
2-Hydroxybiphenyl	1.34
3-Hydroxybiphenyl	4.29
2,2'-Dihydroxybiphenyl	4.08
4,4'-Dihydroxybiphenyl	5.55
2,5-Dihydroxybiphenyl	3.42

TABLE II

CORRECTED RETENTION TIMES IN DICHLOROMETHANE AND MOLAR REFRACTIONS (R_m)

Compound	t (min)	R_m
Toluene	1.07	36.487
Aniline	1.85	42.844
Phenol	1.09	27.999

naphthalene. The effect of structure is even greater with *p*-triphenyl and *p,p'*-tetraphenyl.

The $\ln k$ values for *o*-triphenyl and *m*-triphenyl strongly deviate from the above dependence. These molecules are even more distorted to attain an energy minimum and thus the retention is further decreased. Steric effects are also demonstrated by the retention values for hydroxybiphenyls given in Table I.

The shape of the side chains also exerts an effect on the retention; the retention times decrease in the series *n*-, *sec.*- and *tert.*-butylbenzene in *n*-heptane-dichloromethane as mobile phase.

The effect of substituent polarizability on the retention was studied for the series *o*-xylene, *o*-chlorotoluene and *o*-dichlorobenzene. The results were as expected from the polarizabilities of the given substituents (*o*-xylene, corrected retention volume $V'_R = 1.11$ ml; *o*-chlorotoluene, $V'_R = 2.02$ ml).

A comparison of the retentions of the isoelectronic molecules toluene, phenol and aniline has shown that toluene and phenol are adsorbed to similar extents, in

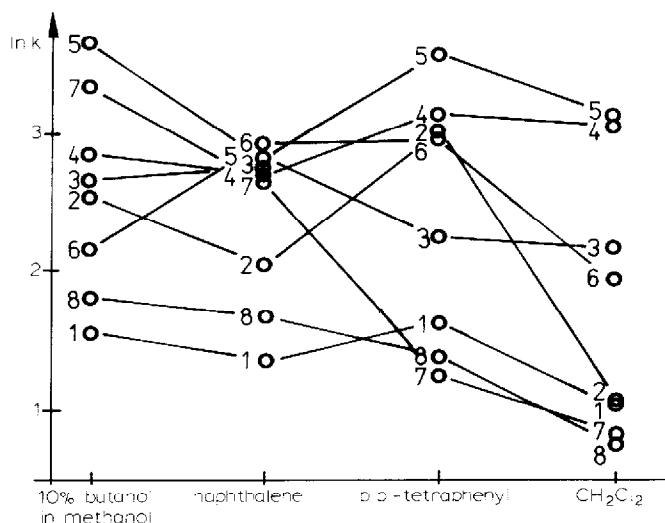


Fig. 6. Changes in retention on going from 10% butanol in methanol to dichloromethane as mobile phase. Solutes: 1 = benzene; 2 = toluene; 3 = *o*-xylene; 4 = *m*-xylene; 5 = *p*-xylene; 6 = 1,2,4-trimethylbenzene (TMB); 7 = 1,2,3-TMB; 8 = 1,3,5-TMB. Solvents: methanol with 10% butanol; methanol, 10% butanol, 10^{-5} M naphthalene; methanol, 10% butanol, 10^{-5} M *p,p'*-tetraphenyl; dichloromethane.

spite of their very different polarities, whereas aniline is much more strongly retained (see Table II). From the retention of nitrobenzene it can be concluded that there is a strong influence of the lone electron pair on the nitrogen which is held much more loosely than the lone electron pairs of oxygen in phenol.

It was found that the carbon sorbent is not completely non-polar and that bonding sites of several kinds are present on its surface. This is illustrated by Fig. 6 which shows the changes in retention times of methyl benzene derivatives with the mobile phases used. It is seen that an addition of aromatics can lead to a modification of the original surface of the adsorbent; competitive sorption occurs, or the sorbate-aromatic complex is bound more strongly to the adsorbent surface.

CONCLUSIONS

Dispersion forces play a major role in the adsorption on the carbon surface. This is demonstrated by the selectivity in separation of positional isomers, especially when small changes in the substituent positions have a large effect on the polarizability or the shape of molecule having the same mass.

The mechanical properties of carbon CF-32-1 fully satisfy HPLC requirements; the particles were not destroyed even at high flow-rates of highly viscous solvents.

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