Journal of Chromatography, 202 (1980) 3–14
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,158

NOVEL POROUS CARBON PACKINGS IN REVERSED-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY*

K. UNGER*, P. ROUMELIOTIS, H. MUELLER and H. GOETZ**
Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität, 6500 Mainz (G.F.R.)

(First received April 24th, 1980; revised manuscript received July 17th, 1980)

SUMMARY

Porous carbon packings of particle size 5–20 μm were prepared by calcination of purified active carbons and cokes having narrow size ranges. Highly efficient columns packed with 10-μm particles were obtained by means of the high-viscosity slurry technique, and exhibited about 3000 theoretical plates at 100 mm length and optimal eluent flow-rate. The loading of columns, $\theta_{0.1}$, was determined to be 25–50 μg of solute per gram of packing. Eluotropic series of solvents were found to be similar to those on pyrocarbon-modified carbons and silicas. The log k' values for homologous compounds increased linearly with the hydrocarbonaceous surface area at constant eluent composition. Studies with polar solutes indicated that the volume polarizability rather than dipole moment was the decisive molecular property of the solute with respect to retention. The successful application of carbon packings in aqueous organic eluents having a pH > 8.5 was demonstrated.

INTRODUCTION

In classical column liquid chromatography, polar adsorbents such as silica and alumina are commonly employed. The reversed-phase mode of modern high-performance liquid chromatography (HPLC), however, requires non-polar adsorbents. Such packings are made by silanization of appropriate silicas with *n*-alkylsilanes. By bonding of *n*-octyl and *n*-octadecyl functional groups to the silica surface its hydrophilic character is greatly reduced. However, the materials still do not behave in a totally hydrophobic manner because their hydrophobic character depends on the type of *n*-alkyl chain bonded and on the surface coverage. The most striking illustration of this fact is the observed chemical instability of reversed-phase packings towards aqueous eluents, which can be attributed to the reactivity of siloxane groups anchoring the *n*-alkyl groups and to the presence of residual silanol groups.

* Presented in part at the 12th International Symposium on Chromatography, Baden-Baden, September 1978.
** Present address: Hewlett-Packard GmbH, Waldbronn, G.F.R.

0021-9673/80/0000–0000/$02.25 © 1980 Elsevier Scientific Publishing Company

In contrast to silica-based adsorbents, active carbon, pyrolytic and graphitized carbon offer a pronounced lipophilic surface. The extent of lipophilic nature can vary widely, depending on the bulk structure and the types of surface functional groups[1,2]. Pure graphite alone possesses a truly non-polar and homogeneous surface due to its structure, and thus can be considered as a model for non-polar adsorbents. Support for this view has been provided by gas adsorption studies and by calculations of adsorbent–adsorbate interactions on graphite[3,4]. Graphite is a soft and non-porous material and is therefore unsuitable for reversed-phase columns which demand mechanically stable packings and a sufficiently large surface area for retention. Some separations in classical LC on active carbon species have been reported[5–8]. The use of these species in HPLC, however, appears highly problematical due to their complex surface composition, the large specific surface area and the presence of micropores.

The first thorough attempts to prepare suitable carbon packings for HPLC were made by Guiochon and co-workers[9–11] by hardening of thermal carbon black agglomerates through pyrolytic decomposition of benzene followed by graphitization. Although extensive retention studies were carried out on these packings, severe problems remained in obtaining sufficient mechanical stability in the 5–10 μm size range. For this reason, these workers performed the pyrolysis of benzene on silica instead of carbon black[12]. A quite different procedure was recently introduced by Plzák *et al.*[13], who reduced polytetrafluoroethylene with alkali-metal amalgams (see also ref. 14). Controlled thermal degradation of polymer beads is another way of producing carbon species[15]. The materials obtained, however, are microporous and small particles in the 5–10 μm size range are expensive to make.

The previously described procedures all require extremely elaborate techniques such as pyrolysis, thermal degradation, etc. Therefore, the primary objective of our study was to find a simpler way of production. Purification and heat treatment of mechanically hard cokes and active carbon species appears to be a promising method. Although our studies are not yet complete and much more research will have to be done to fully characterize the properties of the materials, we present here the first results. After synthesizing suitable materials, retention studies were carried out under reversed-phase conditions to elucidate the specificities in the retention of solutes and to establish the eluotropic strength of solvents. Finally, efforts were made to examine the stability of carbon packings in highly alkaline water–methanol mixtures.

EXPERIMENTAL

Processing of carbon

The starting materials were ground to the desired particle size with a Type Pulverisette 5/2 ball-mill (Fritzsch, Idar-Oberstein, G.F.R.). The two zirconia milling beakers (250 ml volume) were filled with 60 g of carbon material together with six milling beads of 30 mm diameter, also made of zirconia. Optimum milling time for grinding to 5–10 μm particle size was found to be 10 min.

Sizing into narrow 5-μm and 10-μm cuts was performed by a Type Multiplex A 100 MZR zigzag siever (Alpine, Augsburg, G.F.R.). The speed of the rotating wheel was varied in the range of 10,000–18,000 rpm and at a corresponding air flow velocity of 45–37 Nm^3/h. Particle size distribution of the batch was controlled by means of photosedimentation[16].

In order to extract the inorganic impurities the sized carbon materials were subjected to several treatments in the following sequence:

(i) 350 g of material were heated under reflux for 72 h in 1.5 l of hydrochloric acid solution (20%, w/w), then washed with deionized water to remove chloride ions

(ii) 40 g of the resulting material were treated at 430°K with 100 ml of hydrofluoric acid (40%, w/w) in a beaker made of glassy carbon (Sigradur KAZ 26); Sigri, Meitingen, G.F.R.)

(iii) the residue was washed with a hot sodium hydroxide solution to remove ions, washed with deionized water to neutrality and then dried at 473°K.

For heat treatment, 20-g amounts of the purified or native material were placed into cylinders (22 × 120 mm) composed of pure graphite and fitted with a porous screw cap. The graphite cylinders were kindly supplied by Dr. Delle, Kernforschungsanlage, Jülich, G.F.R. The samples were first heated to 473°K for 8 h and then flushed with dry helium. Calcination was carried out at Sigri Elektrographit, Frankfurt/M, G.F.R., using a high-temperature oven (Balzers, Liechtenstein). The oven was first flushed with dry helium and heated at the desired temperature for 2 h. The temperature was varied between 2073 and 3073°K, and the length of treatment was between 5 min and 3 h. After cooling, the samples were removed from the graphite cylinders and stored in glass bottles over helium.

The chemical composition and surface properties of the starting materials and of the intermediate and final products were characterized by the following quantities: elemental analysis of C, H, N and O; ash content; crystallinity as determined by X-ray spectroscopy; particle size distribution by photosedimentation; apparent density due to helium, apparent density due to mercury; specific surface area according to BET[17]; pore volume distribution by mercury porosimetry[17].

Chromatographic measurements

Two types of liquid chromatographs were used, a DuPont Model 830 and a Hewlett-Packard 1084A. Both were operated with a UV detector at 254 nm. Injection volume was 5 μl. The column dimensions were 100 × 4.2 mm, 250 × 4.2 mm and 100 × 10 mm. Column performance was characterized by the dependence of reduced plate height on reduced velocity, the number of theoretical plates, N, obtained under optimal velocity conditions, column resistance factor, φ, and by the peak asymmetry factor, A_s. Quantities measured were calculated using standard equations[18].

RESULTS AND DISCUSSION

Processing and properties of porous carbon

The primary requirement of a packing in HPLC is sufficient hardness, which enables stable packings to be obtained. The previously described pure carbons only partially meet this condition. To overcome this problem we chose hard cokes and active carbons. The refinement of these products involved the following consecutive steps:

(i) milling of starting materials to the desired particle size range

(ii) sizing of ground materials into narrow cuts in the range of 5–10 μm

(iii) purification to remove the non-carbonaceous impurities

(iv) calcination at temperatures above 2073°K to produce an essentially non-polar and homogeneous surface.

Six cokes and active carbons, were selected as starting materials (see Table I) as all have a large bulk crushing strength. The specific surface area spanned more than one order of magnitude from 20 to 869 m^2/g. All products are typical microporous solids except product 5 which additionally possesses some mesopores. Depending on the degree of activation, the carbon content varied between 81 and 91%, w/w. The extraction step described in the Experimental section was thought to remove basic and acidic constituents as well as silica from the crude product when they were accessible to the extracting solvent. Indeed, for product 2 this extraction resulted in an increase of the carbon content from 81.8% to 90.6% whereas the ash content diminished from 10.7% to 3.8%. However, this treatment was not so effective for product 2 (*cf.*, native product 6).

TABLE I

CHARACTERISTICS OF STARTING CARBONACEOUS MATERIALS

No.	*Type*	*Supplier*	S_{BET} (m^2/g)	V_p (*ml/g*)	$d_{app(He)}$ (*g/ml*)	*Carbon content (%)*	*Ash content (%)*
1	Coke	Bergbauforschung, Essen, G.F.R.	20	0.41	—	87.3	7.35
2	Coke	Bergbauforschung	72	0.26	1.83	81.8	10.70
3	Coke	Bergbauforschung	131	0.57	—	81.4	7.10
4	Active carbon	Lurgi, Frankfurt/M, G.F.R.	277	—	—	89.0	1.90
5	Active carbon	Degussa, Hanau, G.F.R.	572	0.94	2.11	90.2	3.30
6	Active carbon	Bergbauforschung	869	0.34	2.02	91.1	2.0

Chromatographic tests with a series of solvent compositions and solutes showed that the extracted carbon products still behave as slightly polar adsorbents. Until now, graphitization or calcination was thought to be the only possible means of creating an inert and non-polar surface. It is well known that not all cokes and active carbons are suitable for graphitization, *i.e.*, the extent of crystallinity of the final product depends on the degree of microcrystallinity of the starting materials[19]. The inorganic impurities may also influence graphitization through the intermediate formation of carbides. This type of catalytic graphitization is often observed but difficult to explain. The rate of graphitization usually becomes noticeably higher above 2200°K, whereas catalytic graphitization generally occurs at lower temperatures. The degree of graphitization, g, can be calculated by

$$g = (3.440 - \bar{d})/0.086$$

where $\bar{d}$ is the mean interlayer spacing of the material derived from X-ray diffraction measurements. $\bar{d}$ is "known to decrease monotonically with the development of the structure from $\bar{d} \geqslant 0.344$ nm in a disordered carbon to 0.3354 nm for near-perfect graphite at room temperature"[20].

All extracted carbons were subjected to graphitization but most work was centered on product 2. Treatment of a batch of extracted carbon 2 having 19.5 μm particle size was carried out at two temperatures, 2673°K and 3073°K. Length of treatment was 2 h. Both products obtained were grey and had a carbon content of 99.5%. Neither oxygen nor nitrogen could be detected by elemental analysis. The ash content was smaller than 0.1%, w/w. The helium density was raised to 2.10 g/ml (3073°K) from 1.83–2.08 g/ml (2673°K). The g value of the extracted product 2 treated at 2073°K for 2 h was calculated to be 0.45. According to this low degree of graphitization the structure of the heat-treated carbon packing resembles more a two-dimensional, disordered structure than a three-dimensionally ordered graphite structure. Therefore it is more precise to designate the products as heat-treated carbons rather than graphitized carbons. Extended calcination studies were also performed on extracted and native active carbon 6. Again the carbon content was above 99.0%. Surprisingly, the apparent helium density after calcination was found to be lower than that of the starting material. Depending on the temperature and length of exposure during calcination, $d_{app(He)}$ ranged from 1.46 to 1.79 g/ml compared to the 2.02 g/ml of the native product 6. This observation is only consistent with the formation of closed pores during calcination which are not accessible to helium.

Heat treatment resulted in a small reduction of mean particle size. For batches of product 6 having $d_{p50} = 9.80$ μm the final particle size decreased to $d_{p50} = 8.9$ μm. The scanning electron micrograph of the product in Fig. 1 shows angular particles with rounded edges. Pore size analysis by means of nitrogen sorption and mercury penetration indicated the presence of mesopores and macropores. No micropores could be detected. The specific surface area of all calcined products ranged between 1–5 m^2/g even at the low calcination temperature of 2073°K. In principle, calcination of extracted or native hard cokes and active carbons yields microparticulate carbon packings with high mechanical stability.

Performance characteristics of carbon columns

Stable and efficient carbon columns could be packed by means of the high-viscosity slurry technique employing a slurry of 17.5% w/w dioxan–paraffin oil (21:79, v/v). The suspension in the packing autoclave was covered with a layer of dry *n*-heptane and forced downwards into the column (100 × 10 mm) at a constant flow-rate of about 10 ml/min. Column performance was represented by plots of reduced plate height, h, *vs.* reduced linear velocity[20]. An example is given in Fig. 2. The shape of the curves is consistent with those obtained on common HPLC packings including reversed-phase materials[21–23]. The minimum value of h occurs at a reduced velocity range $1 < \nu < 10$. Values of the reduced plate height at optimum velocities range from 3.5 to 10 depending on the capacity factor, *i.e.*, the plate height, H, corresponds to 3.5–10 times the mean particle diameter of the packing. Analysis of the log h–log ν dependences of good packed columns in terms of the equation[20]

$$h = B/\nu + A\,\nu^{0.33} + C\,\nu$$

gives values $A = 1.0$, $B = 2.0$ and $C = 0.1$. By curve-fitting using a program kindly supplied by A. Cooke and N. Nelson, Institute of Chemical Analysis and Forensic Science, Northeastern University, Boston, MA, U.S.A., the following values were ob-

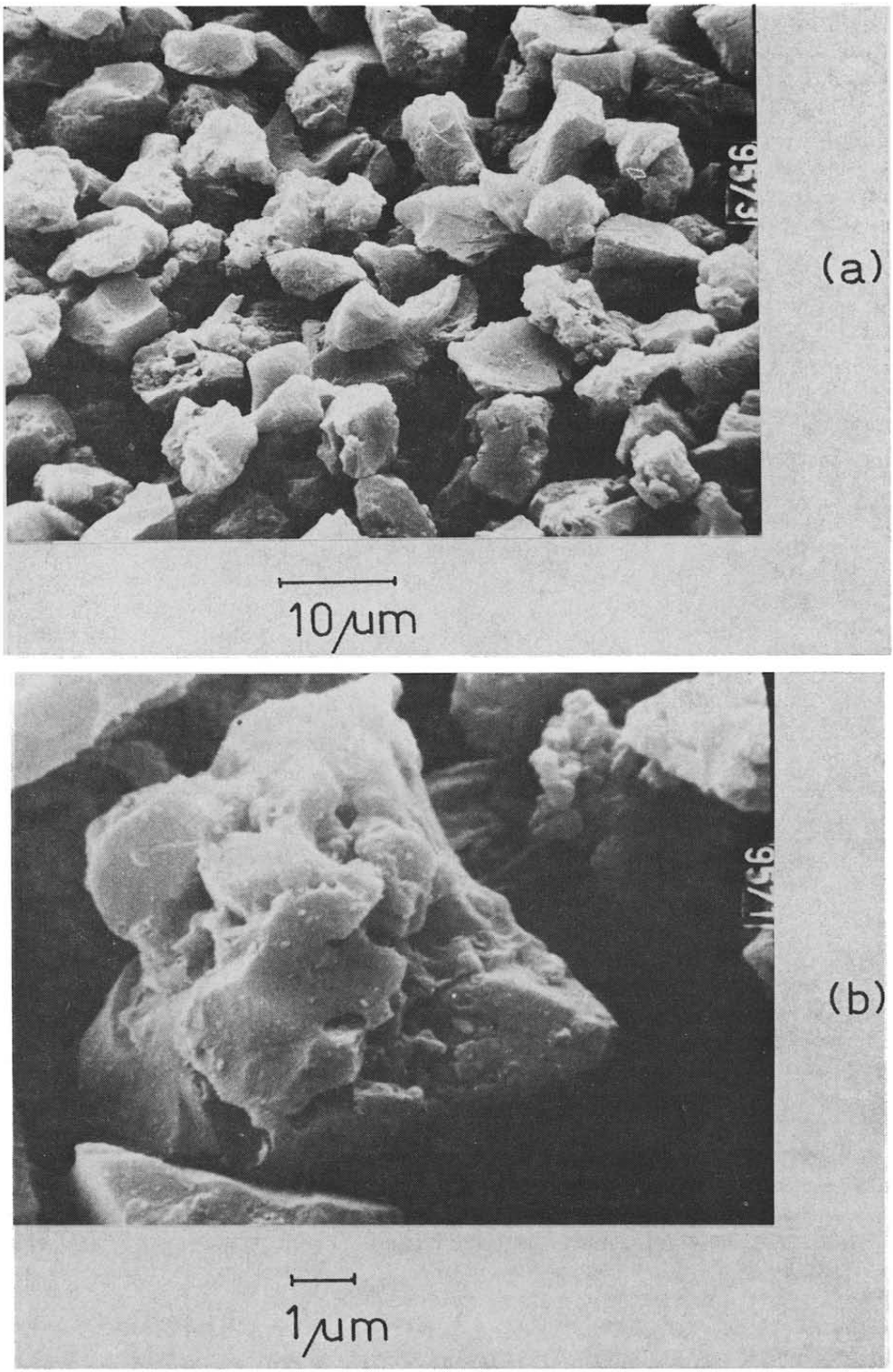

Fig. 1. Scanning electron micrograph of native (a) and calcined (b) (T_c = 2073°K) product 6 having d_p =9.80 µm and 8.90 µm, respectively. Magnification: × 1500 (a); × 7900 (b).

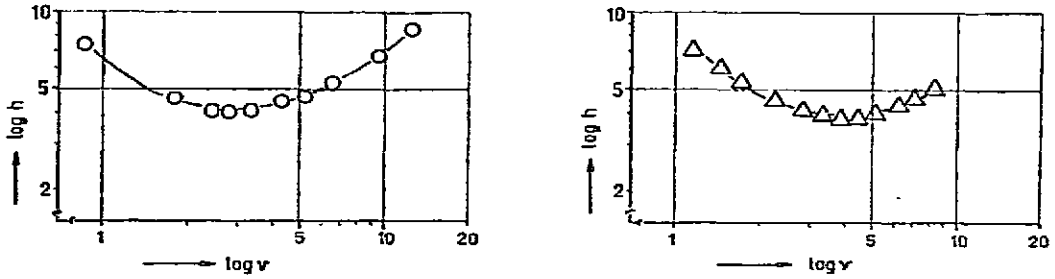

Fig. 2. Dependence of reduced plate height *vs.* reduced velocity on carbon column (100 × 10 mm). Packing: product 6 treated at 2023°K for 5 min; $d_p = 8.9\,\mu m$. Eluent: pure methanol. Solutes: ○, phthalic acid diethyl ester, $k' = 0.22$; △, phthalic acid dibutyl ester, $k' = 0.66$.

tained from Fig. 2: $k' = 0.22$: $A = 0.31$, $B = 5.80$, $C = 0.57$; $k' = 0.66$: $A = 0.09$, $B = 7.48$, $C = 0.48$.

On the 100 × 10 mm column, 2800 (3180) theoretical plates were obtained for the solute having $k' = 0.22$ (0.66) at the minimum in the h *vs.* v curve at a reduced velocity, v, of 2.5 (3.9), which corresponds to a linear flow-rate of $u = 0.37$ (0.44) mm/sec and a volume flow-rate of $f_v = 0.70$ ml/min. The eluent was pure methanol. Column permeability, expressed by the column resistance factor, Φ (ref. 20), which also reflects the quality of the column packing, was 1000–2000 which is at the upper limit of the acknowledge Φ drange of 500–1000. Peak shape was described by the asymmetry factor, A_s, which is defined as the peak width at 0.13 of the peak height divided by the peak width at 0.6 of peak height. Ideal Gaussian peaks have $A_s = 2.0$; for the test solutes, A_s ranged from 2.05 to 2.50.

Particular emphasis was placed on the assessment of the maximum possible loading of carbon columns. On the basis of Snyder's[24] concept of the linear sample capacity, $\theta_{0.1}$, of adsorbents, this quantity is affected by the adsorbent type, the heterogeneity of the adsorbent surface and the specific surface area. $\theta_{0.1}$ is defined as the mass of solute injected per gram of packing that produces a 10% decrease of k'. This amounts to 100–1000 μg/g on bare silica[17] and reversed-phase silica packings[22]. As the specific surface area of the carbon packings is about two orders of magnitude smaller than that of silica packings (3 compared to 300 m^2/g), a $\theta_{0.1}$ value of 10–50 μg/g would be expected. Another frequently used relative measure of maximum column loading is $\theta_{50\%}$, this being the mass of solute per gram of packing which results in a 50% increase in plate height from the extrapolated "zero mass injection"[25]. Colin *et al.*[25] reported values of $\theta_{50\%}$ of 10–350 μg/g on reversed-phase packings and of 10–60 μg/g on pyrocarbon-modified silica packings, the latter having S_{BET} values of 40–80 m^2/g (ref. 26).

Mass loading measurements were carried out on a column (100 × 10 mm) packed with material 6, calcinated at 2073°K for 5 min with $d_p = 8.9\,\mu m$. The eluent was methanol, and 5 μl of solutions of phthalic acid diethyl ester (PEE) and of dibutyl ester (PBE) were injected. The results were: PEE, $k' = 0.22$: $\theta_{0.1} = 50.0\,\mu g/g$, $\theta_{50\%} = 12.5\,\mu g/g$; PBE, $k' = 0.66$: $\theta_{0.1} = 25.0\,\mu g/g$, $\theta_{50\%} = 6.25\,\mu g/g$. The data indicate that the two values of $\theta_{0.1}$ and $\theta_{50\%}$ do not coincide, but that the more retarded compounds exhibit a lower loading compared to the more weakly retarded

compounds, which is consistent with theory. The $\theta_{50\%}$ value is smaller by a factor of 5 compared to pyrocarbon-modified silica and by a factor of 25 in the case of reversed-phase silica packings. This implies that in practical work with carbon packings there must be careful control of the mass of injected solute as well as the use of sensitive detectors.

Retention and selectivity of solutes on carbon packings in reversed-phase chromatography

Assessment of eluotropic series of solvents. The solvent strength parameter, ε^0, as well as the order of solvent strengths (eluotropic series) are useful in selecting a suitable solvent for an analysis in adsorption chromatography.

Neglecting secondary adsorbent effects, the eluotropic strength is defined as[10,28]

$$\log (k'_{i,j}/k'_{i,k}) = A_i(\varepsilon^0{}_k - \varepsilon^0{}_j)$$

where k'_i is the capacity factor, A_i the molecular cross-sectional area of solute i and $\varepsilon^0{}_k$ and $\varepsilon^0{}_j$ the solvent strength parameters of solvents k and j. A_i is obtained by

$$A_i = V_i^{2/3} \cdot N^{1/3}$$

where V_i is the molar volume of solute and N the Avogadro number. Using methanol as reference solvent ($\varepsilon^0 = 0$), the solvent strengths of various solvents were calculated and are listed in Table II. The data indicate that the eluotropic series spans only a small range of ε^0. As expected, aromatics such as benzene and xylene appear to be the strongest solvents. The solvent sequence of the two polynuclear aromatics in Table II is consistent with the findings of Colin *et al.*[10] on pyrocarbon-modified thermal carbon blacks. Large deviations are observed between the eluotropic strength series of non-polar and polar molecules. For instance, tetrachloromethane and methyl sulphoxide act as much stronger solvents for the two polar solutes. The set of data on ε^0 is too limited to develop general guidelines and more work will be carried out on this subject.

The above discussion concerned single solvents as eluents. Much higher selectivity is expected to be provided by binary solvent mixtures. Of these, only water–methanol mixtures up to about 45:55 (v/v) were investigated. By applying the procedure suggested by Scott and Kucera[28] it was found that above this composition the eluent ceases to wet the packing sufficiently. The dependence of the capacity factor of various solutes on the composition of the water–methanol eluent was measured. For all solutes, log k' rises linearly with the water content, in agreement with the results of Colin *et al.*[25] on pyrocarbon-modified silica packings.

Correlation between retention parameters and molecular properties of solutes. Having established the solvent strength series on carbon packings, it is of particular interest to explain the retention of solutes in terms of their molecular properties. It is known for reversed-phase chromatography on silanized silicas that the logarithm of the capacity factor increases linearly with the number of carbon atoms per molecule, or more precisely, with the hydrocarbonaceous surface area of solute, TSA_S, in a homologous series at constant eluent composition[29,30]. A similar behaviour was observed on pyrocarbon-modified silicas and carbon black[25]. The results obtained on our carbon packings (Fig. 3) are consistent with these findings. The compounds studied differ in the number of methyl groups, *e.g.*, methylbenzenes and methyl-

TABLE II

ELUOTROPIC SERIES OF SOLVENTS ON PRODUCT 6 CALCINED AT 2073°K FOR 5 min d_{p50} = 8.9 μm; classification in the order of decreasing capacity factor.

Solvent	ε^0 *for solute*			
	Naphthalene	*Phenanthrene*	*Phthalic acid dibutyl ester*	*2-Naphthaldehyde*
Methanol	—	—	—	—
n-Hexane	0.003	0.018	0.049	0.018
Tetrachloromethane	0.012	0.021	0.038	0.026
Acetonitrile	0.022	−0.006	0.020	0.010
Methyl sulphoxide	0.024	0.031	0.040	0.034
Tetrahydrofuran	0.028	0.030	0.018	0.025
Trichloromethane	0.028	−0.003	−0.004	0.040
Dichloromethane	0.038	0.020	—	0.034
Dioxan	—	0.034	—	0.036
Benzene	—	—	—	—
Xylene	—	—	—	—

naphthalenes, in the number of methylene groups, *e.g.*, phthalic acid esters, and in the number of conjugated aromatic ring systems, *e.g.*, polynuclear aromatics, with the exception of fluorene and fluoranthene. The linearity of the plots for each homologous series is satisfactory, even when positional isomers are included.

The greater slope of the funtion log k' *vs.* TSA_5 for carbon packings compared to silanized silicas can be attributed to their more homogeneous and more hydrophobic surface, lacking polar sites. It should be noted in this context that the specific surface area of carbon packings is smaller by a factor of about 100 than that of silanized silica packings. Under these conditions, the retention of solutes is largely controlled by non-specific dispersion interactions. Thus, the relevant molecular parameter of the solute should be the volume polarizibility rather than the molecular dipole moment. The enhanced retention of aromatic solutes on carbon packings reflects the π-systems of the aromatic rings which permit a high degree of dispersion interaction, particularly when they are favourably positioned at the surface. Polynuclear aromatics composed of more than four conjugated aromatic rings are so retarded in methanol that stronger solvents have to be employed for their elution.

Limited systematic retention studies were carried out with polar aromatic solutes. Table III collects some data obtained for pairs of positional isomers. The *ortho*- and *meta*-derivatives differ in their molecular dipole moments, whereas the volume polarizibilities are approximately equal. The results suggest that there is no obvious relationship between the capacity factor and the molecular dipole moment of the solutes, as observed on reversed-phase silica packings[30]. In the latter case, log k' decreases linearly with the square of the molecular dipole moment at constant volume polarizibility of solute. Further studies, however, are needed to shed more light on the retention of polar solutes on carbon.

Selectivity studies on carbon packings

Carbon packings are well suited for separations of members of homologous series of aromatic compounds due to their pronounced hydrophobic selectivity.

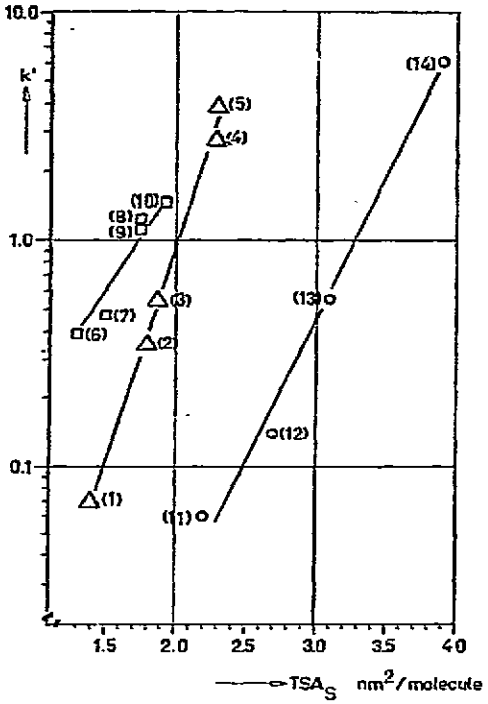

Fig. 3. Logarithm of the capacity factor of solute *vs.* the total hydrocarbonaceous surface area, TSA_S. Column: 250 × 4 mm I.D. Packing: product 2, extracted with HCl and HF, calcined at 3073°K for 3 h; d_p = 6.2 μm. Eluents: methanol for polynuclear aromatics; methanol–water (55:45, v/v) for other solutes. Solutes: 1 = naphthalene; 2 = fluorene; 3 = phenanthrene; 4 = fluoranthene; 5 = pyrene; 6 = toluene; 7 = 1,4-xylene; 8 = 1,2,4-trimethylbenzene; 9 = 1,3,5-trimethylbenzene; 10 = 1,2,4,5-tetramethylbenzene; 11 = phthalic acid methyl ester; 12 = ethyl ester, 13 = butyl ester; 14 = cyclohexyl ester.

Separations were also carried out for aromatic solutes carrying polar functional groups. In the application of carbon packings, particular emphasis was placed on the operation of columns at high eluent pH. A series of alkaloids was employed as test substances in methanol–water mixtures as eluents. The pH of the aqueous phase was adjusted using appropriate buffers. The alkaloids tested were mainly basic substances. Their capacity factors were observed to decrease with increasing pH of the buffer solution. Nevertheless, the selectivity of the carbon packing at pH around 7 was not sufficient to resolve the substances, but improved at pH 11.0–12.0 (Fig. 4). It should be added that this particular column was tested over a period of several months without incurring noticeable loss in efficiency and selectivity.

CONCLUSIONS

The structure of carbon packings varies widely from microcrystalline as in glassy carbons to fibrous and graphite-like, depending on the origin and mode of treatment. Glassy carbons are superior for two reasons: first, the microparticles provide a sufficiently high degree of hardness and mechanical stability; secondly, the

TABLE III

CAPACITY FACTORS AND MOLECULAR PROPERTIES OF SOLUTES

Column: 250 × 4 mm. Packings: a = HCl,HF-extracted product 2 calcined at 3073°K for 3 h, d_p = 6.2 μm; b = as in (a) but d_p = 19.5 μm; c = as in (a) but calcined at 2673°K for 3 h, d_p = 19.5 μm; d = as in (a) but d_p = 5.0 μm. Eluent: water–methanol (45:55, v/v); flow-rate: 1 ml/min. Detector: UV, 254 nm.

Solute	*Volume polarizibility, α* (10^{24} μm³)*	*Molecular dipole moment*[31], *μ (D)*	*k' on column*			
			a	*b*	*c*	*d*
2-Xylene	14.20	0.45	1.40	0.60	0.33	2.86
4-Xylene	14.28	—	1.42	0.62	0.36	3.29
2-Bromotoluene	15.35	1.45	2.74	1.03	0.59	—
4-Bromotoluene	15.40	1.95	2.90	1.17	0.57	—
2-Chlorophenol	16.70	1.43	0.25	0.11	0.09	0.98
4-Chlorophenol	16.81	2.70	0.52	0.18	0.10	1.25
Naphthalene	17.61	—	4.62	2.02	0.70	—
1-Naphthol	18.36	1.39	4.56	1.30	0.26	—
2-Naphthol	—	1.41	3.77	1.00	0.23	—
1-Methylnaphthalene	19.32	0.51	8.59	3.65	1.56	—
1-Nitronaphthalene	20.16	3.87	14.30	4.35	0.82	—
1-Bromonaphthalene	20.37	1.59	—	—	4.03	—

* Calculated by the formula

$$\alpha = \frac{3}{4} \cdot \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M}{\varrho A}$$

where n_D is the refractive index, M the molar mass and ϱ the density of the solute molecule.

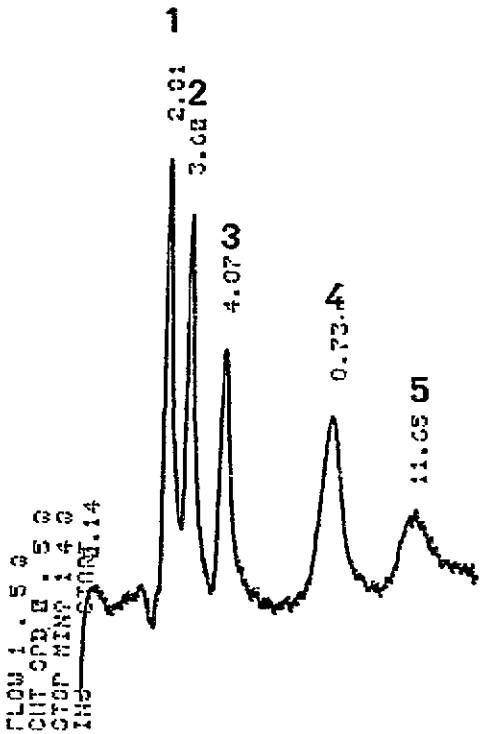

Fig. 4. Separation of alkaloids on porous carbon. Column: 100 × 10 mm. Packing: product 6 calcined at 2073°K for 5 min; d_p = 8.9 μm. Eluent: methanol–water (80:20, v/v) buffered to pH 11.2; flow-rate: 1.5 ml/min. Detector: UV, 254 nm. Injection volume: 25 μl. Solutes: 1 = ephedrine; 2 = codeine + anaestesin; 3 = theobromine; 4 = caffeine; 5 = strychnine.

number of surface defect sites is reduced due to the lower surface area, rendering less likely the formation of polar functional groups on exposure to oxygen.

With regard to their application in HPLC, it is considered unlikely that carbon packings will replace silica-based supports in reversed-phase chromatography and related techniques in the near future. Their chemical inertness and resistance to alkali are, however, advantageous when the particular separation requires an aqueous organic solvent of pH >7.0 as eluent.

ACKNOWLEDGEMENT

We gratefully acknowledge the assistance of Dr. Tillmanns, Sigri Elektrographit, Griesheim.

REFERENCES

1 H. P. Boehm, *Angew. Chem.*, 78 (1966) 617.
2 B. R. Puri, in P. L. Walker, Jr. (Editor), *Chemistry and Physics of Carbon*, Vol. 6, Marcel Dekker, New York, 1971, pp. 191–282.
3 S. Ross and J. P. Olivier, *On Physical Adsorption*, Wiley-Interscience, New York, 1964, p. 270.
4 A. V. Kiselev and Y. J. Yashin, *Gas-Adsorption Chromatography*, Plenum, New York, 1969.
5 D. A. Hill and A. Tiselius, *Acta Chem. Scand.*, 5 (1951) 854.
6 R. S. Alm, *Acta Chem. Scand.*, 6 (1952) 1186.
7 M. A. Jermyn, *Aust. J. Chem.*, 10 (1957) 55.
8 S. I. Yeh and H. L. Frisch, *J. Polym. Sci.*, 27 (1958) 149.
9 H. Colin, C. Eon and G. Guiochon, *J. Chromatogr.*, 119 (1976) 41.
10 H. Colin, C. Eon and G. Guiochon, *J. Chromatogr.*, 122 (1976) 223.
11 H. Colin and G. Guiochon, *J. Chromatogr.*, 137 (1976) 19.
12 H. Colin and G. Guiochon, *J. Chromatogr.*, 126 (1976) 43.
13 Z. Plzák, F. P. Dousek and J. Jansta, *J. Chromatogr.*, 147 (1978) 137.
14 E. Smolková, J. Zima, F. Dousek, J. Jansta and Z. Plzák, *J. Chromatogr.*, 191 (1980) 61.
15 R. Kaiser, *Chromatographia*, 3 (1970) 38.
16 K. K. Unger and M. G. Gimpel, *J. Chromatogr.*, 180 (1979) 93.
17 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, New York, 1967.
18 L. R. Snyder and J. J. Kirkland, *Introduction to Modern Liquid Chromatography*, Wiley-Interscience, New York, 1980.
19 D. B. Fischbach, in P. L. Walker (Editor), *Chemistry and Physics of Carbon*, Vol. 7, Marcel Dekker, New York, 1971, pp. 1–106.
20 P. A. Bristow and J. H. Knox, *Chromatographia*, 10 (1977) 279.
21 K. Unger, W. Messer and K. F. Krebs, *J. Chromatogr.*, 194 (1978) 1.
22 K. Unger, P. Roumeliotis and W. Liebald, to be published.
23 J. H. Knox and A. Pryde, *J. Chromatogr.*, 112 (1975) 171.
24 L. R. Snyder, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968, pp. 77–98.
25 H. Colin, N. Ward and G. Guiochon, *J. Chromatogr.*, 149 (1978) 169.
26 G. Guiochon and H. Colin, *Chromatography Review*, Vol. 4, No. 2, *Spectra Physics, Santa Clara, CA*, 1978, p. 2.
27 L. R. Snyder, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968, pp. 186–239.
28 R. P. W. Scott and P. Kucera, *J. Chromatogr.*, 142 (1977) 213.
29 C. Horvath and W. Melander, *International Laboratory*, Nov./Dec. 1978, p. 11.
30 P. Roumeliotis and K. K. Unger, *J. Chromatogr.*, 149 (1978) 211.
31 A. L. Mc Clellan, *Tables of Experimental Dipole Moments*, Freeman, San Francisco, CA, 1973.