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COMPARISON OF MESOPOROUS CONTROLLED-POROSITY GLASSES TO SILICA GEL AS SOLID SUPPORTS FOR C_{18} CHEMICALLY BONDED PHASES

Z. SUPRYNOWICZ*, B. BUSZEWSKI, R. LODKOWSKI and A. L. DAWIDOWICZ
Department of Chemical Physics, Institute of Chemistry, Maria-Curie Sklodowka University, 3 Maria Curie Sklodowska Square, 20-031 Lublin (Poland)

SUMMARY

A series of packings with chemically bonded C_{18} phases has been prepared using controlled-porosity glasses with various boron contents on the surface. Based on the physicochemical and chromatographic properties, such packings are compared with those prepared from commercial silica gels. Special attention is paid to the possibility of practical application of packings prepared from mesoporous controlled-porosity glasses.

INTRODUCTION

Increasing demands for more complex analyses by high-performance liquid chromatography (HPLC) increases the requirements of column packings as regards their mechanical, thermal and solvolytic resistance. The silica gels are most often used as the supports of chemically bonded phases, nevertheless controlled-porosity glasses (CPGs) may also be used owing either to the possibility of obtaining controlled-porosity structures or relatively greater thermal and solvolytic resistance[1–8].

As regards their chemical properties, porous glasses or more strictly the starting material used to prepare such glasses belong to the group of hard glasses characterized by a relatively high boron oxide content. This is related to the chemical composition of the starting material which contains 4–15% sodium oxide, 18–60% boric oxide and 40–85% silica[2–6]. During the successive stages of CPG production, heating of the starting material in order to separate the two phases, silica and sodium–boron, and leaching of the latter and simultaneous removal of a secondary porous subphase, a siliceous skeleton is formed containing a small amount of boron (up to 6%, w/w boric oxide)[2,9,10].

Experimental investigations showed that, owing to secondary heating of CPGs at temperatures above 673 K, a possibility exists of controlling the enrichment of the glass surface in boron atoms[11–14] leading even to the appearance of B_2O_3 clusters[15,16], which is very important in the context of the preparation of special packings with chemically bonded C_{18} phases owing to the greater film rigidity[6,23] and greater chemical stability of the B–OH boronyl bond formed in comparison to the Si–OH silanol bond[15–17].

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Continuing the investigations initiated in the Department of Chemical Physics, Institute of Chemistry, Maria Curie-Skłodowska University[2–7,10] on the preparation of packings with chemically bonded phases for gas chromatography (GC) and HPLC, we have chemically modified the surfaces of two different types of supports, *i.e.*, CPG and silica gel and the packings prepared were evaluated by means of physicochemical and chromatographic measurements. The novetly of this work consists in the application of mesoporous CPG instead of wide-pore CPG having controlled contents of surface boron atoms, which has permitted greater effective surface areas for sorption exchange comparable to those attainable in the case of packings produced on the basis of silica gel. The results obtained were compared to those obtained for sorbents with chemically bonded C_{18} phases produced from silica gels having different porous structures.

The mean pore diameter of CPG depends on the time and the temperature of the preliminary thermal treatment of the initial material. Mesoporous CPGs are obtained by heating Vycor glass at lower temperatures over a short time. Under conditions the demixing process is not complete. As a result, the final porous product obtained after leaching at low temperature is rich in residual boron and has an high content of sodium atoms. For this reason it is very difficult to compare such mesoporous glasses with previously discussed macroporous ones[5,6,23]. The secondary thermal treatment of such material will bring about the enrichment of its surface in boron and first of all in sodium atoms.

EXPERIMENTAL

Materials and reagents

Small CPG particles, $d_p = 8.7\ \mu m$, were produced according to the procedure described earlier[18]. Enrichment was carried out at 893 K for 2, 20, 50 and 116 h. The heated materials were then rehydroxylated according to the procedure described elsewhere[7].

Two silica gels, *i.e.*, LiChrosorb Si 60, $d_p = 8.3\ \mu m$, and LiChrosorb Si 100, $d_p = 9.2\ \mu m$, were used in comparative investigations. For chemical modification, octadecyldimethylchlorosilane (ODMCS) (Petrarch Systems, Bristol, PA, U.S.A.), specially prepared morpholine[19] (Reachim, Moscow, U.S.S.R.) serving as an activator and dried toluene[20] (POCh, Gliwice, Poland) were used. The reaction was carried out in glass ampoules excluding contact of the reagents with the environment. The method, mechanism and conditions of reaction were described previously[19,21].

For preparation of binary eluents in the reversed-phase (RP) HPLC system, methanol (POCh) and water purified according to the procedure described in ref. 22 were used. All solvents were of analytical grade purity.

Physico-chemical and chromatographic measurements

The measurements of the specific surface area, S_{BET}, mean pore diameter, D, and pore volume, V_p, of CPG and silica gel supports were carried out by the nitrogen sorption method using sorptomatic apparatus Model 1800 (Carlo Erba, Milan, Italy). The sodium concentration was estimated by means of an Hilger and Watts atomic absorption spectrometer.

The density of coverage was calculated on the basis of Berendsen–de Galan equation[24] utilizing elemental analysis data. For this purpose, a CHN analyzer Model 185 (Hewlett-Packard, Palo Alto, CA, U.S.A.) was used.

A LC 20 liquid chromatograph equipped with an UV detector (Pye Unicam, Cambridge, U.K.) operating at 254 nm was used. The samples were injected by means of a 7120 valve (Rheodyne, Berkeley, CA, U.S.A.) using a 10-μl sample loop. The results were recorded with a TZ-4200 recorder (Laboratorní Přístroje, Prague, Czechoslovakia).

The pH values of aqueous suspensions of bare CPGs and silica gels containing 5% (w/w) of solid were measured with an OP-201/1 pH-meter (Radelkis, Budapest, Hungary) according to Engelhardt and Müller[25].

The stainless-steel columns (100 mm × 4 mm I.D.) (Chemical Reagents Factory-ZOCh, Lublin, Poland) were packed under a pressure of 45 MPa according to a modified ascending slurry method described by Buszewski *et al.*[26]. The slurry consisted of 8% (w/w) packing material in tetrachloromethane–methanol (90:10). Methanol was used as a driving solvent.

The dead volume, V_0, was determined on the basis of solvent peaks according to the method described by Buszewski[19].

RESULTS AND DISCUSSION

The two types of materials, *i.e.*, CPG and silica gels, differ not only in chemical composition (CPG surface was additionally enriched in boron atoms) but also in internal porous structure. Physicochemical characteristics of bare CPG and silica gels are listed in the Table I.

The selection of materials possessing identical porosity parameters is very difficult or even impossible[19,26–28]. Even if two of the four parameters D, V_p, S_{BET} and pore shape have similar values, the other two will differ significantly. For this reason, we have used as reference systems two different silica gels.

Considering the individual materials in Table I, it is seen that the starting porous glass is characterized by a pore diameter, bulk density and specific surface

TABLE I

PHYSICOCHEMICAL CHARACTERISTICS OF BARE SILICA SUPPORTS

S_{BET} = Specific survace area; D = mean pore diameter; V_p = pore volume; ρ_s = bulk density; pH of 5% aqueous suspension. Subscripts 0–116 denote number of hours of enrichment.

No.	*Support*	*Abbreviation*	*Porosity*			ρ_s	*pH*
			S_{BET} (m^2/g)	D (nm)	V_p (cm^3/g)		
1	LiChrosorb	Si 60	335	8.5	0.86	0.42	7.07
2	LiChrosorb	Si 100	268	13.2	1.19	0.37	6.90
3	Controlled-porosity	CPG_0	334	8.1	1.26	0.44	6.15
4	glasses	CPG_2	299	8.6	0.87	0.412	7.15
5		CPG_{20}	271	8.2	0.99	0.414	7.40
6		CPG_{50}	275	8.8	1.38	0.42	7.70
7		CPG_{116}	331	8.9	1.34	0.39	7.95

area comparable to those of LiChrosorb Si 60 silica gel, however the pore volume increases significantly after heating. The second parameter permitting the distinction of these materials is the pH value of their aqueous suspensions. The suspension containing porous glass (Table I, support 3) has significantly acidic properties, as expected considering that B–OH groups, being more acidic than Si–OH silanol groups, exist on the glass surface. The changes in physico-chemical properties of mesoporous glasses caused by secondary thermal treatment are non-conventional. The small increase in pore diameter with increasing heating time has been discussed many times in the literature. This increase is connected with the crystallographic changes occurring in the silica skeleton of CPG. Interpretation of the changes in pore volume, specific surface area and bulk density is more difficult. As was mentioned, the porous glass used for the synthesis was prepared by means of melting and leaching of the initial glass sodium–boron–silicon. It appears that the conditions used are not sufficient to achieve complete melting. The siliceous skeleton remaining after leaching of such glass contains a relatively large amount of sodium, 1.32% of sodium oxide, in comparison to CPGs obtained after complete and correct melting, 0.03–0.05% of sodium oxide. It is known from the literature data that thermal treatment of the porous glass leads to diffusion of boron and sodium atoms from the interior of the silica skeleton onto the CPG surface. In our case the enrichment of the surface in sodium atoms causes an increase in basicity (pH, Table I) and a change in the chemical nature of the surface. In the case of porous glass, the surface area occupied by a single nitrogen molecule used to determine the specific surface area may appear incorrect.

The maximum density of coverage, (α_{RP}), for column packings prepared on the basis of CPGs occurs for CPG_{20}–C_{18}, *i.e.*, at the point corresponding to extremum of their specific surface area changes (Table I). Such an extremum did not occur in our previous investigations on macroporous CPGs, for which the specific surface area diminished during prolonged secondary thermal treatment[5,6]. Thus, according to the results of our earlier work it seems that after 20 h of secondary heating of CPG, maximum and optimum enrichment of the surface in boron atoms is achieved, which permits maximum coverage density (α_{RP}, Table II).

TABLE II

CHARACTERISTICS OF THE PACKINGS WITH CHEMICALLY BONDED C_{18} PHASE

Types of packings denoted as in Table I. nRP = number of alkylsilyl ligands per nm^2.

Column No.	*Type of packing*	*Coverage density*		
		% C	*α_{RP} ($\mu mol/m^2$)*	*nRP (nm^{-2})*
1	LiChrosorb Si 60-C_{18}	20.3	3.45	2.08
2	LiChrosorb Si 100-C_{18}	18.8	3.85	2.33
3	CPG_0-C_{18}	17.39	2.80	1.69
4	CPG_2-C_{18}	17.09	3.06	1.84
5	CPG_{20}-C_{18}	18.22	3.65	2.24
6	CPG_{50}-C_{18}	14.96	2.81	1.69
7	CPG_{116}-C_{18}	17.36	2.82	1.70

Prolonged heating of CPG, 50 and 116 h, leads to increased melting with formation of the sodium–boron–silicon glass structure, increased specific surface area and to less satisfactory chemical bonding parameters (Table II).

In the case of wide-pore glasses prepared by means of prolonged thermal treatment, which contained less than 0.05% sodium oxide, the coverages obtained were significantly higher[5,6,10,18].

The ten-fold higher sodium level in the siliceous skeleton in comparison to conventionally prepared CPG may result in greater diffusion of sodium in relation to boron than that in the case of conventionally prepared porous glasses. This problem is relatively complex because a significant rôle is played not only by the relative concentrations of the individual elements remaining in the CPG structure, but also by the ionic diameters of these elements, coordination numbers, diffusion rates, temperature, etc.

Fig. 1 shows that all the porous glasses prepared exhibit significantly narrower pore size distributions than do the silica gels. Porous glasses possess more homogeneous structures in respect of the pore diameter. From Fig. 1 it is seen that thermal treatment leads to an increase in this homogeneity. On the other hand one cannot exclude the presence and formation of some micropores during the preparation of mesoporous CPG, as evidenced by the asymmetric course of hysteresis loops in adsorption isotherms determined for CPG_0 (curve 3 in Fig. 2). Although from the shape and location of the hysteresis loop one cannot draw important conclusions, the above suggestions however are supported by the results of our earlier investigations which indicated that the heterogeneity of the CPG surface is due probably to the presence of micropores[2,3].

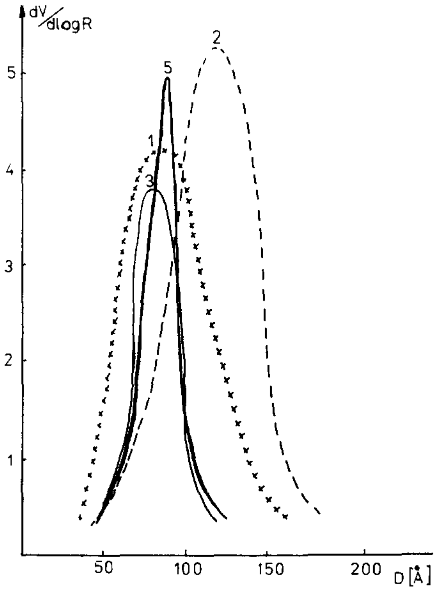

Fig. 1. Pore-size distribution for the unmodified sorbents (1) LiChrosorb Si 60, (2) LiChrosorb Si 100, (3) CPG_0 and (5) CPG_{20}. V = pore volume, R = pore radius, D = pore diameter.

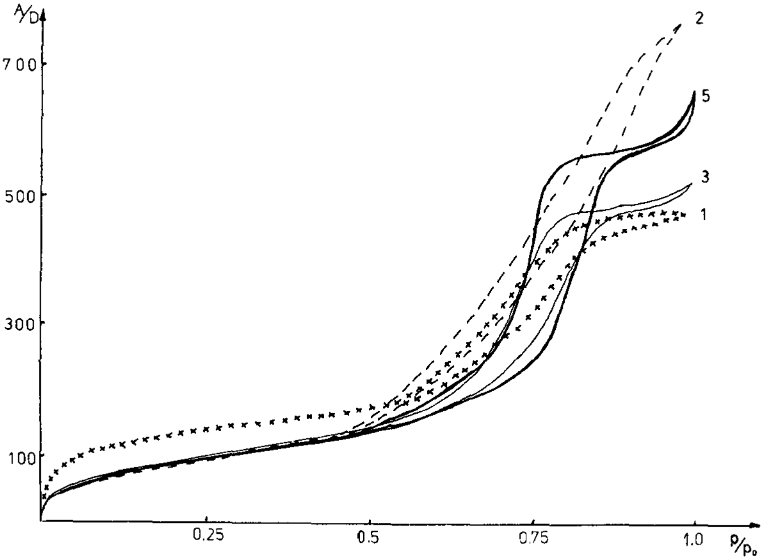

Fig. 2. Adsorption–desorption (A/D) isotherms of nitrogen. Notations as in Fig. 1. p/p_0 is the relative pressure of adsorbate (N_2).

In spite of the above reservations, one can state that even at low coverage density the chromatographic separations performed on the sorbents prepared on the basis of porous glasses are comparable or even better than those obtained on sorbents prepared on the basis of silica gel (Fig. 6).

Some parameters characterizing the quality of these packings[29,30] are listed in Table III. The columns investigated are characterized by similar and sufficiently high numbers of theoretical plates, $h \approx 5$, and relatively low working pressures, ψ 500–1500. The asymmetry coefficients, f_{As}[29,30], for both packings prepared on the basis of silica gel as well as for CPG_2 and CPG_{20} have typical values, 0.9–1.25. It is interesting that f_{As} correlates well with α_{RP}. Some peak tailing on CPG_0, CPG_{50} and

TABLE III

CHARACTERISTICS OF THE 100 mm × 4 mm I.D. COLUMNS WITH METHANOL–WATER (70:30, v/v) AS THE MOBILE PHASE

Solute: naphthalene. n_T = Number of theoretical plates; h = reduced height equivalent to a theoretical plate; HETP, φ = flow resistance coefficient; f_{As} = asymmetry factor.

Column No.	k'	n_T	h	φ	f_{As}
1	5.3	2216	4.05	1370.2	1.15
2	3.6	1940	4.95	1321.3	1.08
3	5.55	2070	4.80	1897.1	1.44
4	5.25	2170	4.60	1210.8	1.25
5	4.49	2560	3.90	1298.1	1.17
6	3.20	2350	4.25	1211.2	1.28
7	4.60	2260	4.42	1218.1	1.31

CPG_{116} may be caused by possible changes in chemical composition and by an increase in surface energy (see also the adsorption–desorption isotherms in Fig. 2). These effects may be intensified owing to non-uniformity of the coverage. Also of note is the highest number of theoretical plates, n_T, on the columns packed with CPG_{20} containing chemically bonded C_{18} phase and generally higher values of the capacity factor, k', in comparison to the k' values obtained on LiChrosorb Si 100 (Table III).

Considering the relationships between α and x presented in Fig. 3 one can conclude that:

(i) LiChrosorb Si 60 and LiChrosorb Si 100 -C_{18} show similar shapes of the α *vs.* x relationship, which differ however from those of the relationships obtained for all CPG-based C_{18} packings

(ii) the lowest, but similar, separation selectivity, *i.e.*, similar hydrophobicity over a relatively wide range of mobile phase (methanol–water) composition was obtained for the packings prepared on the basis of LiChrosorb Si 100 and CPG_{20} (curves 2 and 5).

(iii) the highest selectivity for the packings produced on the basis of CPG is attainable over a significantly narrower range of mobile phase composition (sharp maxima may indicate another retention mechanism) than in the case of silica gels (more rigid alkyl chain film)[6,23].

The second effect is also evident in the relationship between log k' of phenol and benzene and the mobile phase composition on packings characterized by

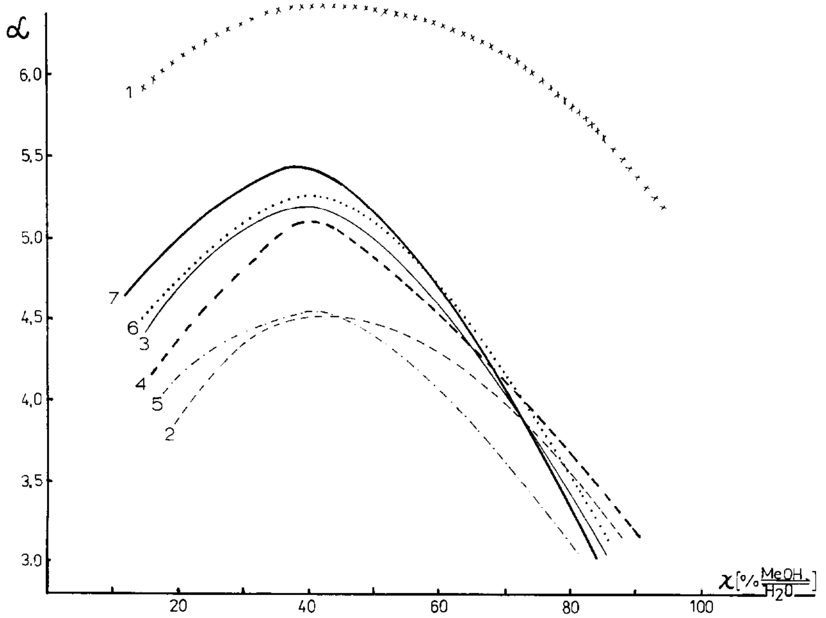

Fig. 3. Dependence of the separation selectivity, $\alpha = k'_{benzene}/k'_{phenol}$ on the mobile phase composition. Curves: (1) LiChrosorb Si 60-C_{18}; (2) LiChrosorb Si 100-C_{18}; (3) CPG_0-C_{18}; (4) CPG_2-C_{18}; (5) CPG_{20}-C_{18}; (6) CPG_{50}-C_{18}; (7) CPG_{116}-C_{18}.

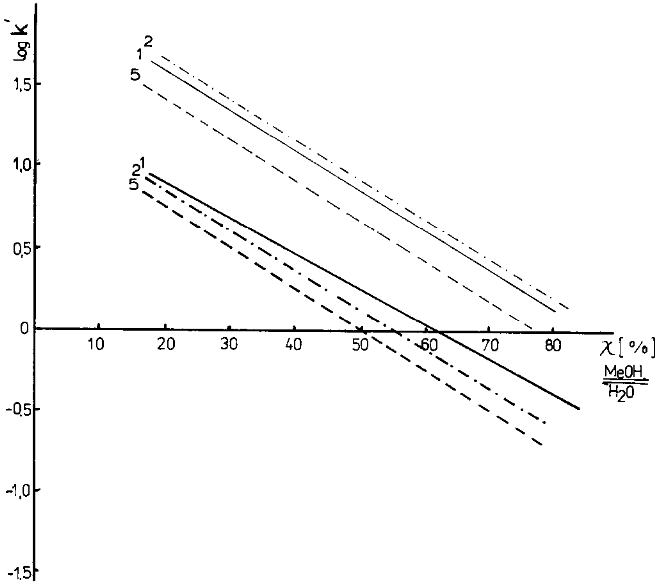

Fig. 4. Dependence of k' for phenol (thick lines) and benzene (thin lines) on the mobile phase composition on (———) LiChrosorb Si 60-C_{18}, (– · – · –) LiChrosorb Si 100-C_{18} and (– – – –) CPG_{20}-C_{18}.

similar coverage densities, α_{RP} = 3.45–3.85 μmol/m^2 (Fig. 4). The small differences resulting from the coverage densities have little influence on the retention and selectivity in the case of non-polar compounds (parallel lines). The linear plot for the polar phenol on LiChrosorb Si 60-C_{18} has a different slope (thick line 1). This may be caused by stronger or weaker interactions of the narrow-pore LiChrosorb Si 60 surface unblocked by alkylsilyl ligands, with the phenol molecules, which behave as Bronsted acids in aqueous solutions. Small differences in S_{BET} and α_{RP} values in the case of materials 2 and 5 (Table I and II) are reflected in small changes of retention and capacity ratios (Table III).

From Fig. 5, it is seen that significantly higher values of normalized retentions occur on LiChrosorb Si 60-C_{18} and CPG_0-C_{18} because of the higher effective surfaces in the column (see S_{BET} in Table I). The changes in normalized retentions for the alkylbenzene series are most similar for LiChrosorb Si 100-C_{18} and CPG_{20}-C_{18} (Fig. 5, lines 2 and 5). When the enrichment time is longer than 20 h, decreased retention of alkylbenzenes is observed (Fig. 5, lines 6 and 7).

Fig. 6 shows a comparison of the separation of a mixture of aromatic hydrocarbons on the sorbents characterized by comparable coverage densities, α_{RP}. The longest retention times and total analysis time are found on the column packed with LiChrosorb Si 60-C_{18} (A). Also, in the case of LiChrosorb Si 100-C_{18}, the peak show slight asymmetry. A complete separation characterized by most symmetric peaks and the shortest analysis time is obtained on the column packed with CPG_{20}-C_{18}. A more detailed knowledge of the spongy structure of bare CPG obtained by simultaneous application of more precise physico-chemical methods, as well as the improvement of the technology of these materials in respect of the melting process,

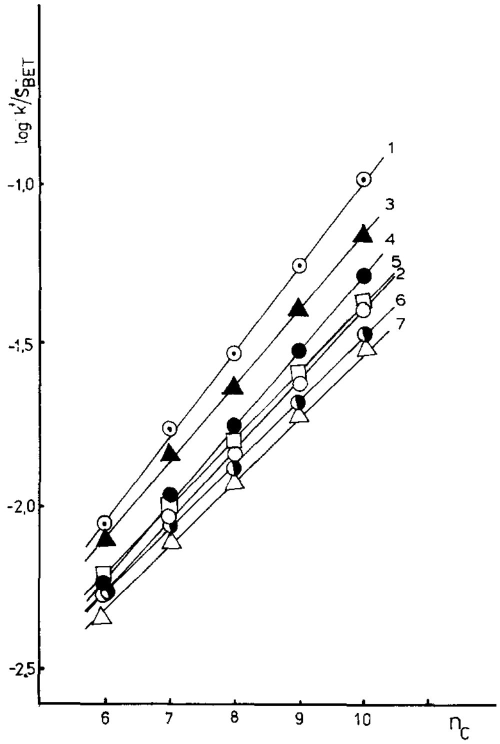

Fig. 5. Dependence of log k'/S_{BET} on the number of carbon atoms in alkylbenzene molecules, n_C, on 1 (⊙) LiChrosorb Si 60-C_{18}, 2 (○) LiChrosorb Si 100-C_{18}, 3 (▲) CPG$_0$-C_{18}, 4 (●) CPG$_2$-C_{18}, 5 (□) CPG$_{20}$-C_{18}, 6 (◑) CPG$_{50}$-C_{18} and 7 (△) CPG$_{116}$-C_{18}.

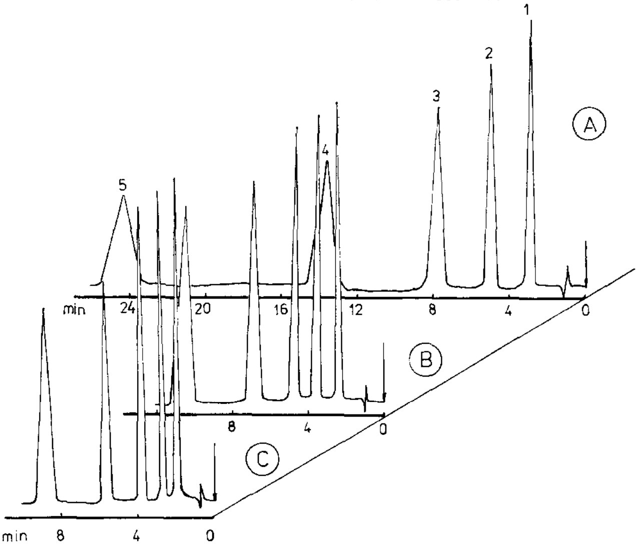

Fig. 6. Separation of an alkylbenzene mixture on (A) LiChrosorb Si 60-C_{18}, (B) CPG$_{20}$-C_{18} and (C) LiChrosorb Si 100-C_{18}. Peaks: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = propylbenzene; 5 = butylbenzene.

permitting strictly defined porosity parameters, will have important cognitive or practical effects. The presence and contribution of micropores as well as the contents of boron and sodium atoms in the surface layer should be precisely evaluated and controlled.

CONCLUSIONS

Some HPLC packings produced on the basis of mesoporous CPGs show similar physico-chemical structure to that of LiChrosorb-based reference systems.

The secondary thermal treatment of our CPG leads to non-conventional changes in pore volume and specific surface area (minimum S_{BET} for CPG_{20}).

The pore-size distribution of CPG is narrower than that of LiChrosorbs.

Mesoporous CPG-based sorbents are characterized by lower coverages of C_{18} chemically bonded stationary phase (excluding CPG_{20}) than the analogous column packings based on Lichrosorbs.

Retention data of for non-polar solutes are relatively high (Table III).

The comparison of the effective surface layer on C_{18} CPGs is predominantly influenced by the mobile phase composition, and the curves of α *vs.* x are more convex.

The surface boron and sodium atom concentrations must be determined in order to evaluate the quality of the preparation.

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