

Siliceous sorbents with immobilized Carbowax 20M as column packings for liquid chromatography

I. Physico-chemical properties of siliceous materials with immobilized Carbowax 20M layer

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ABSTRACT

For better stability the gas chromatographic stationary phase Carbowax 20M is often immobilized on different support materials. Some physico-chemical properties of siliceous supports with thermally immobilized Carbowax 20M are described. The results obtained point to the formation of acidic groups (centres) in the Carbowax layer during its immobilization procedure.

INTRODUCTION

The polyethylene glycol (PEG) Carbowax 20M is one of the most popular stationary phases used in gas chromatography (GC) [1–3], mainly from its very high selectivity towards many organic compounds. For instance, Carbowax 20M and all PEGs are superior to methylsilicone stationary phase for the separation of polar compounds differing only slightly in boiling temperatures [4]. The main disadvantages of Carbowax 20M result from its low thermal stability and low resistance to the destructive action of oxygen [1,2,4,5]. To minimize these shortcomings, various immobilization procedures are used. Thermal immobilization was described by Aue and co-workers [6–8]. In addition to the preparation conditions, they formulated a hypothesis concerning the mechanism of the bond-

ing of a Carbowax 20M chain to the siliceous surface [8,9].

Several years ago, Aue and co-workers' method was applied to the modification of controlled-porosity glasses differently enriched in boron atoms [10–12]. The sorbents obtained were characterized by means of the adsorption isotherms calculated from the GC data. A model of Carbowax 20M bonding, in agreement with that suggested by Aue and co-workers, was proposed [11]. It was also demonstrated that sorbents with thermally immobilized Carbowax 20M can be used as fillings of columns for HPLC [12]. These sorbents are characterized by good selectivity and reproducibility of capacity factors. They can be used for many analytical purposes, e.g., in the analysis of phenols, steroids and benzodiazepines [12,13].

In spite of all earlier investigations, still very little is known about the structure of the immobilized Carbowax 20M layer and about the properties and application of such sorbents,

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especially in HPLC. The aim of this work was to obtain some physico-chemical and chromatographic properties of Carbowax 20M and to shed some more light on the structure of the immobilized layer.

The first part of this paper concerns the physico-chemical properties of sorbents with a Carbowax layer. These sorbents are compared with the initial materials (applied as supports of the investigated phase) and sorbents with adhesively deposited Carbowax 20M.

The second part considers mainly the chromatographic properties of chosen sorbents used as packings for (A) liquid adsorption chromatography in normal- and reversed-phase systems and (B) gel permeation chromatography. Additionally, sorbents with Carbowax 20M are compared with LiChrosorb DIOL, a sorbent of similar polarity. Finally, the properties of sorbents before and after chromatographic examination are discussed.

EXPERIMENTAL

Materials

Controlled-porosity glasses (CPGs) were prepared from Vycor-type glass consisting of 55% SiO_2 , 35% B_2O_3 and 10% Na_2O . Separate portions of this material (120–150- μm fractions) were converted into porous form by appropriate thermal treatment and leaching in sulphuric acid and sodium hydroxide solution. The details of the CPG preparation procedure have been described elsewhere [14,15]. In order to obtain packings for HPLC columns, porous glasses were additionally crushed and from the ground material a fraction of about 8 μm was collected. Table I gives the physico-chemical properties of the prepared porous glasses (called CPG II and CPG III) and LiChrosorb Si-100 silica gel (Merck, Darmstadt, Germany). Carbowax 20M was bonded to all the siliceous materials as described [6,7,16,17]. Finally, the following materials were obtained: CPG II C; CPG III C and Si-100 C (where C represents the presence of bonded Carbowax 20M).

After the preparation procedure (but before the HPLC column packing procedure) the sorbents obtained were placed in a stainless-steel

column (300 x 8 mm) thermostated at 60°C and washed with 250 ml each of hexane, chloroform and methanol at a flow-rate of 1 ml/min.

Methods

Specific surface area measurements were carried out using a Sorptomatic 1800 instrument (Carlo Erba, Milan, Italy). Mean pore diameters of the prepared sorbents were calculated on the basis of nitrogen adsorption-desorption hysteresis curve measured with the same instrument.

The amounts of bonded Carbowax 20M were calculated utilizing elemental analysis data. For this purpose a Model 185 CHN analyser (Hewlett-Packard, Palo Alto, CA, USA) was used.

Particle size fractionation was carried out using a Multi-Plex Laboratory Classifier 100 MZR (Alpina, Germany).

Potentiometric titrations were performed using an automatic titrator set (Radiometer, Copenhagen, Denmark). A PHM-64 digital pH meter with a G 202 C glass electrode and a K 4018 calomel reference electrode were used together with standard thermostated vessels. Titrations were carried out using 0.1 M NaOH and 0.1 M HCl at 298 ± 0.5 K in a nitrogen atmosphere; 0.1 M NaCl was used as the supporting electrolyte. For each point on the potentiometric titration curve the equilibrium state with respect to the display of the pH meter was achieved. The surface charge density was evaluated as described elsewhere [18].

X-ray patterns of the investigated materials were obtained on a DRON-3 diffractometer using a Cu $K\alpha$ radiation lamp with a nickel filter.

RESULTS AND DISCUSSION

Table I gives the physico-chemical properties of two porous glasses CPG II and CPG III and LiChrosorb Si 100 silica gel. In addition to values of the specific surface areas (S_{BET}) and pore diameters (D_{max}) corresponding to the maximum of the pore-size distribution function, the values of the pore volumes ($V_{\text{p}}^{\text{ads}}$) and mean diameters ($D_{\text{c}}^{\text{ads}}$) calculated from the desorption (top rows) and adsorption (bottom rows) branches of the

TABLE I

PHYSICO-CHEMICAL PROPERTIES OF THE MATERIALS USED AS SUPPORTS OF IMMOBILIZED CARBOWAX 20M

S_{BET} = Specific surface area; D_{max} = pore diameter corresponding to the maximum of the pore size distribution function; V_p^{des} and D_c^{des} = pore volumes and mean diameters calculated from desorption (top rows) and adsorption (bottom rows) branch of the nitrogen isotherm.

Support	S_{BET} (m ² /g)	V_p^{des} (cm ³ /g)	D_c^{des} (Å)	D_{max} (Å)
CPG II	228	1.01	180	150
		0.98	170	
CPG III	347	1.16	134	100
		1.13	131	
Si-100	318	1.32	165	140
		1.26	160	

nitrogen isotherm are also given. D_c values were calculated assuming that the pores had cylindrical shapes. Table II gives the related physico-chemical values for the sorbents obtained by immobilization of Carbowax 20M on CPG II and CPG III and on silica gel Si-100. The values of the amount of the polymer calculated per gram of the support or per square metre of its surface are also given. On the basis of the latter values, the thicknesses of the Carbowax layers (d_t) were calculated assuming that the density of Carbowax is 1.33 g/cm³.

As can be seen, the physico-chemical prop-

erties of the initial siliceous materials are very similar to one another. It was our intention to choose similar sorbents and to demonstrate that there is no essential difference whether silica gel or porous glass of similar properties is used as a support.

The similar values of D_c^{des} and D_c^{ads} and of V_p^{des} and V_p^{ads} indicate that there are no bottle-shaped pores. The materials with immobilized Carbowax 20M possess much lower specific surface areas and pore volumes; however, these data should be treated with some reserve, because in the calculations the same values were assumed for the areas occupied by a single adsorbed molecule (nitrogen) on pure siliceous surfaces and on supports with immobilized Carbowax. In addition, it is not certain whether nitrogen dissolves in the polymer layer to some extent. The D_{max} values for sorbents with immobilized Carbowax 20M are slightly lower than those for the initial sorbents. This is related to the presence of a Carbowax layer on the surface of the pores. The mean diameters D_c are larger for the sorbents with immobilized Carbowax 20M because the smallest pores are probably filled with polymer. The amount of immobilized Carbowax 20M is highest for CPG II C, which is especially evident when w/S values are taken into account. The values of w/S for CPG III C and Si-100 C are almost the same.

As was mentioned in the Introduction, Carbowax 20M possesses a low thermal stability, especially in the presence of oxygen. It is com-

TABLE II

PHYSICO-CHEMICAL PROPERTIES OF THE SORBENTS WITH IMMOBILIZED CARBOWAX 20M

w/w and w/S = polymer amounts calculated per gram and per square metre of the support; d_t = thickness of the Carbowax layer; other parameters as in Table I.

Sorbent	S_{BET} (m ² /g)	V_p^{des} (cm ³ /g)	D_c^{des} (Å)	D_{max} (Å)	w/w (×100) (g/g)	w/S (×100) (g/m ²)	d_t (Å)
CPG II C	57	0.37	250	130	58.58	0.256	19.2
		0.35	240				
CPG III C	92	0.39	175	100	53.49	0.154	11.6
		0.38	170				
Si-100 C	119	0.62	210	130	46.80	0.147	11.1
		0.61	205				

monly known that even a minimum content of oxygen in the carrier gas can cause oxidation and destruction of the Carbowax layer used as a stationary phase in a GC column [5]. It may lead to the formation of aldehyde, carboxyl [1,4,19] and oxirane groups [20] and consequently can change the surface properties. Similar phenomena may occur during thermal immobilization. Therefore, the modified materials were investigated in order to check whether such processes took place during their preparation procedure. For this purpose the potentiometric titration method was applied.

Potentiometric titration of a suspension of a solid provides much information about the structure and character of a solid surface [21], mainly about the charge surface density (a) on the solid surface-electrolyte interface. Potentiometric titration of the following materials was performed: porous glass (CPG III), porous glass with immobilized Carbowax 20M (CPG III C), porous glass with adhesively deposited Carbowax 20M (CPG III C_{adh}) (with the same amount of stationary phase as for the materials with an immobilized Carbowax layer) and, for comparison, bulk Carbowax 20M and bulk Carbowax 20M additionally heated in a nitrogen atmosphere at 270°C (*i.e.*, at the same temperature as during the immobilization process). For both heated and non-heated Carbowax 20M the titration curves coincided with that obtained for the titration of pure electrolyte. This means that the samples possess zero charge in the investigated pH range. For the other samples values of the surface charge density (a) were calculated according to ref. 18. Adhesively deposited Carbowax 20M dissolves in the electrolyte and probably only a monolayer of the polymer remains on the surface of porous glass, so the σ values were recalculated per gram of glass support, Q . Fig. 1 shows the Q vs. pH dependences for the three samples, (A) CPG III, (B) CPG III C_{adh} and (C) CPG III C.

In the pH range 2.5-5.5, CPG III and CPG III C_{adh} are characterized by virtually zero charge. Above pH 5.5 a gradual increase in negative charge is observed, suggesting the presence of acidic groups. The negative charge Q increases slightly quicker for CPG III than for CPG III

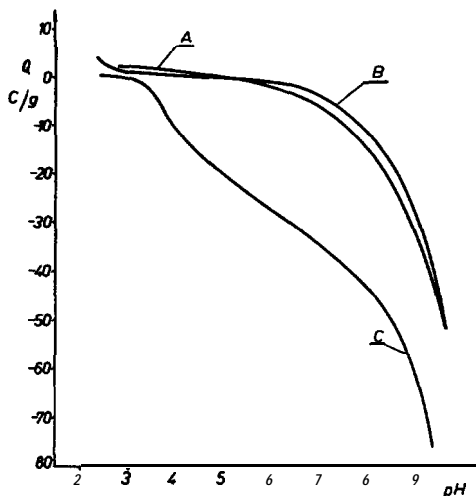


Fig. 1. Charge surface density vs. pH recalculated per gram of the support, Q , for (A) CPG III, (B) CPG III C_{adh} and (C) CPG III as a function of pH.

C_{adh} . This may result from the presence of the surface Carbowax layer which remains after dissolution of the excess amount of the deposited polymer. The course of curve C in Fig. 1 (glass with thermally immobilized Carbowax 20M) is completely different from those for curves A and B. The segment parallel to zero charge density is very short and at pH 3.5 a rapid increase in negative charge is observed, indicating the presence of strongly acidic groups. From pH 4 to about 8 a monotonic increase in negative charge is seen, suggesting the presence of several surface acidic groups of different strengths ranging from pK 4 to 8. It is probable that the mechanism of bonding of these groups (carboxyl?) to the surface is different, e.g., by being attached directly or through the chains of various lengths. Similar shapes of the curves have been observed in the case of oxidized activated carbons [22]. The changes in the surface charge connected with the acidic groups being created during the immobilization process can be better presented as the difference (ΔQ) between the values for materials with thermally immobilized and adhesively deposited Carbowax 20M (Fig. 2). The rapid increase in the charge at pH 3.5 indicates a relatively high content of strongly acidic (pK 3.5) groups. This may mean that some of them are very close or even are clustered. From the

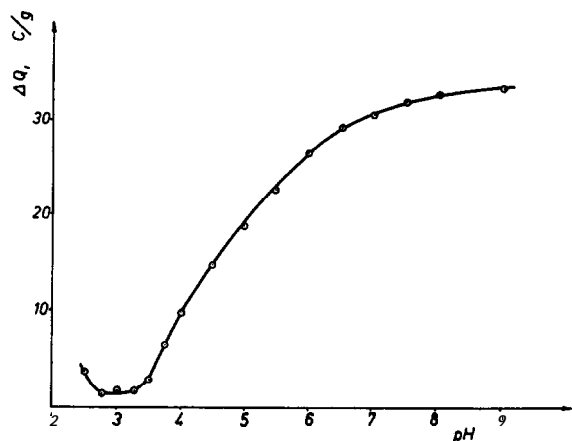


Fig. 2. Difference ΔQ between the surface charge densities recalculated per gram of the support for the material with thermally immobilized Carbowax 20M (see Fig. 1, curve C) and the material with adhesively deposited Carbowax 20M (see Fig. 1, curve B).

change in the surface charge and from the amount of the polymer, it is possible to estimate that one monoprotic acidic group lies every 40-mers ($\text{CH}_2\text{CH}_2\text{O}-$) in the Carbowax chain.

As was mentioned above, thermal immobilization of Carbowax 20M causes the partial oxidation and degradation of the polymer chain. It can be expected that carboxyl, aldehyde and oxirane groups are created. Moreover, it seems that not only temperature (270°C) and traces of oxygen are the main factors causing the formation of dissociating groups. The catalytic influence of the siliceous surface is very significant, as shown by the fact that Carbowax 20M heated at 270°C in the same nitrogen atmosphere but without the presence of silica does not show any ionic groups; as already mentioned, the titration curves for heated Carbowax and the electrolyte overlap one another.

In order to obtain additional information about the structure of the Carbowax layer immobilized on a siliceous surface, the X-ray patterns for Carbowax 20M, porous glass with an immobilized Carbowax 20M layer, porous glass with adhesively deposited Carbowax layer and pure porous glass supports were obtained (Fig. 3). The X-ray pattern for porous glass CPG III does not show any diffraction peaks because of the amorphous structure of the material. The

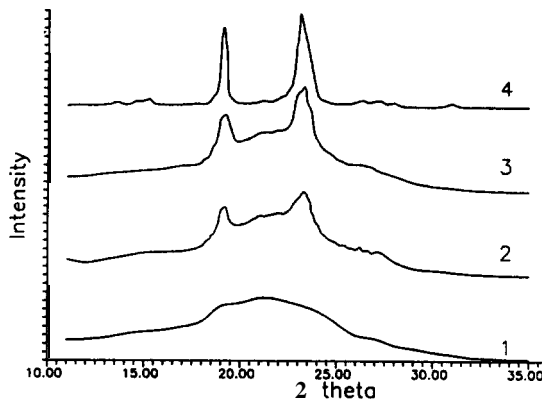


Fig. 3. X-ray diffraction patterns for: (1) CPG III, (2) CPG III C, (3) CPG III C_{adh} and (4) Carbowax 20M. The intensity of the X-ray diffraction patterns for Carbowax has been decreased about H-fold.

diffractogram of Carbowax 20M possesses two strong peaks at $2\theta = 19.1^\circ$ and 23.2° . The same peaks are observed in the X-ray patterns of porous glass with immobilized and adhesively deposited Carbowax 20M (CPG III C and CPG III C_{adh}). It can be concluded that part of the immobilized and also part of the adhesively deposited Carbowax 20M are in a crystalline form, just as in bulk Carbowax. This means that some of the Carbowax 20M chains in the materials CPG III C and CPG III C_{adh} are positioned parallel. Quantitative diffraction analysis revealed about 4 wt.% of a crystalline form in CPG III C and about 5% in CPG III C_{adh} , which after recalculation gives about 11.5% and 14.5% of a crystalline form in immobilized and adhesively deposited Carbowax layers, respectively.

In contrast to the results obtained by **potentiometric** titration, from which different properties of materials with immobilized Carbowax and those with adhesively deposited polymer can be deduced, the X-ray patterns do not exhibit any essential differences between these materials.

CONCLUSIONS

Thermal immobilization of Carbowax 20M leads to changes in the physico-chemical properties of the initial material.

Potentiometric titration indicates the presence of acidic groups in the layer of immobilized

Carbowax. This suggests a destruction process in the polymer during immobilization. In addition to oxygen and temperature, the catalytic influence of the siliceous surface seems to be a very important factor in Carbowax degradation.

Part of the immobilized Carbowax 20M exists in a crystalline form as in the bulk Carbowax.

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