A STUDY OF THE SORPTION PROPERTIES OF THE "SPHEROSILS"

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SUMMARY

Spherosil (with the commercial name "Porasil") is one of the most specific adsorbents and its application is widened by its use in gas chromatography. It is based on porous silica beads, and is able, because of the hydroxyl groups on its surface, to interact specifically with molecules that contain a dipole or π electrons. To evaluate its sorption character, the behaviour of benzene, n-hexane and cyclohexane was followed, *i.e.*, that of sorbates with the same number of carbon atoms but with different structures. Attention was paid to the activation conditions and to the dependence of the sorption character on changes in specific surface area. It was important to decide to what degree the concentration of the surface hydroxyl groups varies with changes in the specific surface area. The measurement and evaluation of adsorption isotherms were carried out by the frontal chromatographic technique, using Spherosils with four different surface areas. It is concluded from the calculated absolute adsorption isotherm that, in the series of Spherosils studied, a change in the geometrical surface area and possibly in the porosity play a predominant role while the concentration of hydroxyl groups on the surface is approximately constant.

INTRODUCTION

Considerable attention has been paid in recent years to the development of new solid adsorbents for gas chromatography (GC). These are chiefly various types of porous polymers or adsorbents based on silica, with defined surface areas and pore sizes. It has been shown that these materials have advantages from the point of view of analytical applications. In contrast to the earlier use of common adsorbents in the analysis of mainly permanent gases and low-boiling substances, these materials can be used in a much more general way; in some cases, their properties are more favourable than those of the common stationary phases. For the wider use of these materials, both as adsorbents in gas–solid systems and as supports in gas–liquid systems, information on their interactions with the gaseous phase is needed, and papers have been published on this aspect[1-9].

While it is still unclear to what extent adsorption, diffusion and dissolution

participate in porous polymer interactions, porous adsorbents based on silica may be considered to be much better defined materials from the point of view of these interactions. In an investigation of these new materials, experience gained from studies of various types of silica gel and of their geometrical or chemical modifications may be used[1-11].

The firm of Péchiney-Saint-Gobain, France, has developed a type of porous silica beads with the name "Spherosil", and these are distributed by Waters Associate Inc., U.S.A., under the commercial name "Porasil"[12,13]. Some papers[1-8] have already been devoted to the study of the importance of Spherosils in GC, dealing with both analytical applications in the separation of polar and non-polar substances and some physico-chemical properties of this material. As, for analytical applications of Spherosils, it is important to know the effect of the activation temperature, the specific surface area and the porosity on the course of a separation process, our studies on this topic are reported in this paper.

EXPERIMENTAL

Spherosil is chemically pure silica with smooth-surfaced grains with a particle size from several to 300 μm. It is chemically inert. Each type of Spherosil is characterized by the total pore volume, the specific surface area and the pore distribution independent of the grain size.

TABLE I

PROPERTIES OF THE SPHEROSILS USED IN THIS WORK[6]

Commercial designation of Spherosil	Mean pore diameter (nm)	Specific surface area (m²/g)	
		By nitrogen	By benzene
XOC 005	5000	8	12.1
XOB 015	1180	25	22.6
XOB 030	490	66	54.3
XOA 400	< 100	428	258

Four types of Spherosil were used, the characteristics of which are given in Table I (ref. 15). The sorption measurements were carried out with the vapours of benzene, n-hexane and cyclohexane. For evaluation of the sorption character, these sorbates were used because they each have the same number of carbon atoms and close boiling points (69–81°) but, depending on the nature of the adsorbent, they can interact either specifically or non-specifically with its surface owing to their different geometrical structures and electronic configurations.

All experiments were carried out with the Fractovap Model C chromatograph (Carlo Erba) with a thermal conductivity detector.

The columns used were glass tubes, 4 mm in diameter, containing the following weights of Spherosils: 7.0862 g of specific surface area 8 m²/g; 6.5827 g of specific surface area 25 m²/g; 8.0235 g of specific surface area 66 m²/g; and 1.3754 g of specific surface area 428 m²/g. Carefully dried nitrogen was used as the carrier gas at a flow-rate of 75 ml/min throughout.

The Spherosils were activated directly in the chromatograph in a stream of dry nitrogen at 100° for 4 h. The measurements were carried out by the frontal technique at 70°.

RESULTS AND DISCUSSION

In an effort to work with material that was as well defined as possible, attention was first devoted to the activation of the Spherosils. For this reason, differential thermal analysis of all four adsorbents was carried out. From the recordings (Fig. 1), it follows that a sharp change in weight occurs at 100°, corresponding to the desorption of water from the Spherosil surface. From 100° up to 450°, the maximum temperature in this study, the weight of the adsorbent slightly and uniformly decreases, owing to the removal of more water. It cannot yet be decided unambiguously whether this water is liberated as a result of the formation of hydrogen bonds or by the dehydroxylation of the surface with the formation of siloxane groups, or whether it is water bound by co-ordination bonds. According to the latest literature data[14], it can be assumed that, during the activation, the water bound by hydrogen bonds is released first, with the formation of an inner hydrogen bond (Fig. 2). With a further increase in the temperature, the water molecules bound by co-ordination bonds to silicon are probably liberated, and finally the condensation of hydroxyl groups with the formation of siloxane bonds occurs. This mechanism is not, however, adequately supported
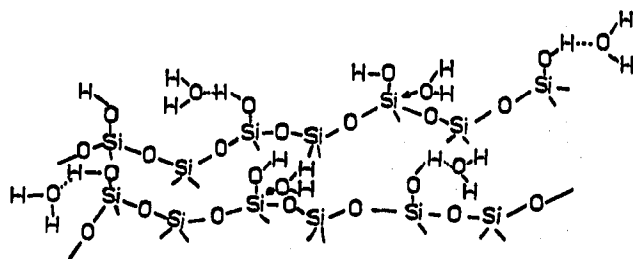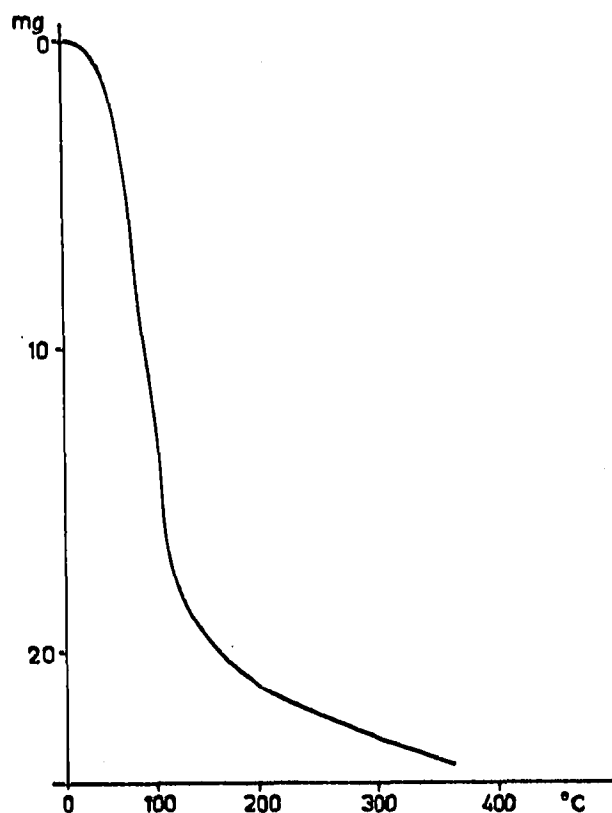

Fig. 1. Differential thermal analysis graph for Spherosil with a specific surface area of 66 m²/g.

Fig. 2. Surface structure of porous silica beads.

TABLE II

ELUTION TIMES OF *n*-HEXANE, CYCLOHEXANE AND BENZENE ON SPHEROSILS

Commercial designation of Spherosil	Elution times (sec)		
	n-Hexane	Cyclohexane	Benzene
XOC 005	23.5	24	39
XOB 015	32	33	116
XOB 030	93	92	555
XOB 400	88	87	367

by experimental data and the authors intend to deal with this problem in a future paper.

According to the KISELEV classification[10], Spherosil is an adsorbent of the second type. It can, therefore, interact specifically with molecules that contain π-electron bonds, *i.e.*, with benzene in the present case. The elution data for *n*-hexane, cyclohexane and benzene, given in Table II, clearly support this type of interaction. GUILLEMIN[5], who followed the dependence of the sorption of *n*-butane and butene-1 on the surface area of Spherosil, found anomalies within the range 30–50 m²/g; he tried to explain them by assuming a change in the adsorbent structure in this specific adsorption range and by a change in the concentration of hydroxyl groups. His conclusions are, however, not entirely authoritative and they disagree on some points. For this reason, measurement with benzene vapour was carried out in the present work, which should show a much more marked effect of changes in the concentration of surface hydroxyl groups.

For a quantitative description of the adsorption process, with its dependence
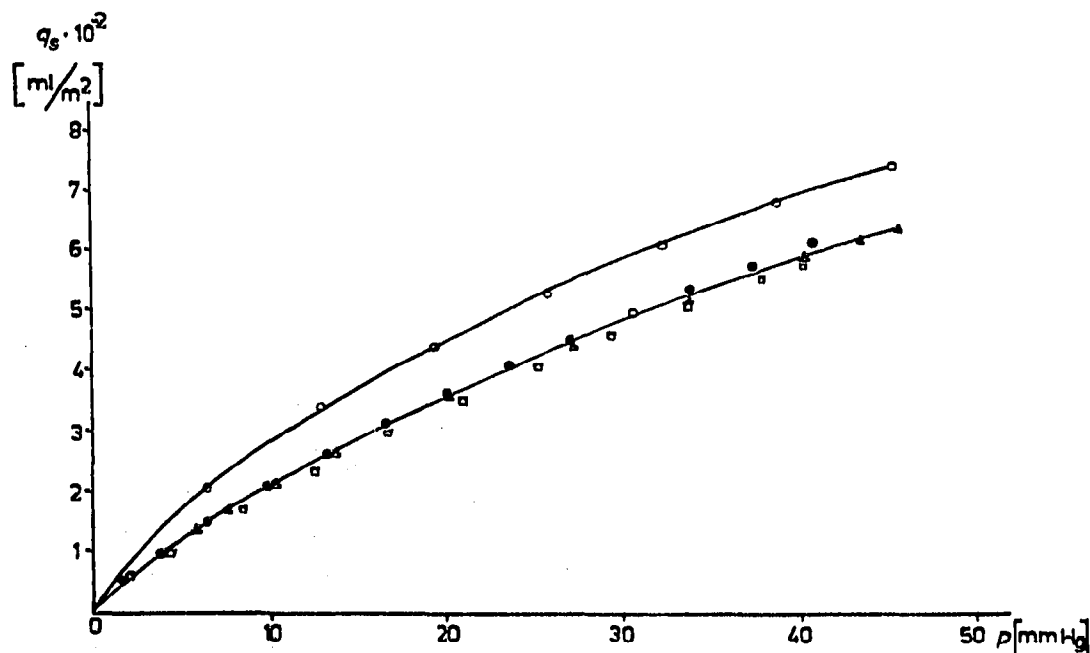

Fig. 3. Adsorption isotherms for benzene on Spherosils with the following specific surface areas: □, 12.1 m²/g; △, 22.6 m²/g; ●, 54.3 m²/g; ○, 258 m²/g.

on the specific surface area, adsorption isotherms were measured by the frontal technique on Spherosils with specific surface areas of 8, 25, 66 and 428 m²/g, and the amounts adsorbed were recalculated to those per 1 m² of the adsorbent surface. From Fig. 3, in which the results of these experiments are shown, it follows that the shape of the isotherms is essentially identical for Spherosils with specific surface areas of 8, 25 and 66 m²/g, while for the Spherosil with a specific surface area of 428 m²/g the amounts adsorbed are substantially higher.

The amounts adsorbed per 1 m² of the surface show that the surface structures of the three types of Spherosil of less absorption are very similar and that the surface concentrations of the functional groups are approximately the same. The changes in the amounts adsorbed per 1 g of the adsorbents are therefore caused only by the change in the geometrical surface area of the adsorbents.

The situation is, however, different with the fourth Spherosil type that was studied, with a specific surface area of 428 m²/g. It is clear from Fig. 3 that the surface concentration of benzene is, in this case, higher than for the previous types. This difference might indicate an increase in the concentration of hydroxyl groups on the adsorbent surface.

From the point of view of the sorption process, the porosity of the material must also be taken into consideration. From Table I, in which the producer's data are given, it follows that Spherosils having essentially identical adsorption isotherms are materials with wide pores, while the Spherosil with the specific surface area of 428 m²/g can be characterized as a narrow-pore material. It can be said in general that capillary condensation occurs with wide-pore materials only at relative pressures approaching unity[9,10]. Because the present work was carried out at rather low relative pressures (up to 0.1), it is justifiable to assume that the above process could not affect the adsorption process. Since work at high relative sorbate pressures need not be considered in GC, it can be concluded that in the case of wide-pore Spherosils only the surface concentration of hydroxyl groups is decisive for the chromatographic process.

Adsorption on the narrow-pore Spherosil studied is, however, affected by capillary condensation which can take place at low relative pressures[10]. It can then be presumed that in this case capillary condensation is the main cause of the increased surface concentration of benzene observed. It will be necessary to verify in detail to what extent a possible change in the surface concentration of hydroxyl groups contributes to this increase.

GUILLEMIN[5] found that, in the case of the sorption of butene-1, anomalies occur in its dependence on the surface area for specific surface areas in the range 30–50 m²/g, and he explained this phenomenon by a change in the concentration of the so-called reactive hydroxyl groups taking part in the adsorption of substances with π-electron bonds. His results were related to unit weight of the adsorbent, whereas in the present work the results were recalculated to one surface area unit so that direct comparison of the different various Spherosil types was possible. During the calculations, the values of the specific surface areas given by the producer, which were determined by the sorption of nitrogen, were not used; rather, the values measured in the present paper by the adsorption of benzene were used (see Table I). The data treated in this way did now show any anomaly similar to that found by GUILLEMIN. Hence, the values given by GUILLEMIN were re-calculated to one surface area unit, both for the
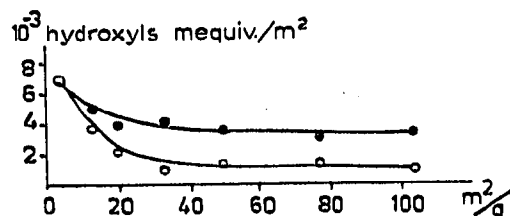
Fig. 4. Dependence of the surface concentration of hydroxyl groups on specific surface areas. O, reactive hydroxyls; ●, total hydroxyls.

reactive hydroxyl group concentration and for the total hydroxyl group concentration (Fig. 4). In both cases it was found that for the Spherosil with a specific surface area of 20 or 30 m^2/g the hydroxyl group surface concentration is essentially constant. This concentration increases with a decrease in the surface area. If, however, we take into account errors to which the measurement of especially small surface areas by the static method is subject, and the fact that GUILLEMIN carried out the chromatographic measurement with a compound with a completely different structure from that of the compound used for the surface area determination, even the total hydroxyl group concentration on small surface areas can be considered to be essentially constant. This fact is in accordance with our experimental results and with the conclusions drawn from them.

Since Spherosil is a relatively new sorbent, it is, from the point of view of its analytical use, important to carry out further experiments in order to elucidate the sorbent–sorbate interaction.

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