

NOVEL POLYORGANOSILOXANE XEROGELS WITH BIFUNCTIONAL $\equiv\text{Si}(\text{CH}_2)_3\text{SH}/\equiv\text{Si}(\text{CH}_2)_3\text{NH}_2$ SURFACE LAYER

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Abstract

Novel polyorganosiloxanes gels with bifunctional $(\equiv\text{SiCH}_2)_3\text{SH}/\equiv\text{Si}(\text{CH}_2)_3\text{NH}_2$ surface layer have been prepared by a sol-gel technique using silane-ternary systems. The surface properties of the obtained gels are highly reproducible. The effect of the addition of a catalyst was investigated, and it is shown that the addition of fluoride ion has a highly beneficial effect on the porous properties of the materials. The synthesized samples have specific surface areas up to 250 m²/g, and have a high potential as selective sorbents for heavy and noble metals (Hg²⁺, Ag⁺, Au³⁺ etc.).

Introduction

Sulfur-functionalized silica adsorbents attract much attention because of their ability to adsorb selectively ions of noble and heavy metals. The selectivity of these adsorbents is much higher as compared with the oxygen- and nitrogen-containing analogues. Moreover, sulfur-functionalized silica has an application in chromatography for separation of optical isomers and for excretion of enzymes and nucleic acids. They are also convenient for immobilization of biologically active compounds. In addition, the irreversible adsorption of stable metal complexes with fixed sulfur-containing ligands on a porous support presents an opportunity for use in heterogeneous catalytic systems [1-4]. Organosilanes can be considered as ideal precursors for the synthesis of functionalized silicas, as their chemical composition is widely variable. Organosilanes, contained both S- and N-functions, are therefore very suitable for the synthesis of selective adsorbents with both chemical functions. The selectivity and capacity of these adsorbents towards noble metal ions will largely depend on the number and functionality of the N- and S-functions [1].

So far the studies have mainly dealt with the post-synthesis modification of silica by grafting a variety of organosilanes to the surface [1-4]. This approach, however, has a number of disadvantages. Firstly, the surface loading, which may be achieved, is limited by the amount of hydroxyl groups on the surface. Especially in the case of fumed silica, this concentration is relatively low. Secondly, the design of the functionalized surface by grafting methods required several separate stages. Therefore, the one pot synthesis of such adsorbents is highly appealing. Such synthesis may be made by using of sol-gel technique, polymerization and gelation of the selected organosilanes [5-6]. In this way, one should be able to obtain not only a high surface concentration of active groups, but this approach allows one also to introduce simultaneously the various functional groups. Thus, this approach opens wide (and new) opportunities for controlled surface design. In this work, we will describe the

sol-gel synthesis of polysiloxane adsorbents with aminopropyl $[-(\text{CH}_2)_3\text{NH}_2]$ and mercaptopropyl $[-(\text{CH}_2)_3\text{SH}]$ surface groups.

Experimental

3-aminopropyltriethoxysilane $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$ (APTES; 99%, Aldrich); 3-mercaptopropyltrimethoxysilane $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{SH}$ (MPTMS; 95%, Aldrich); tetraethoxysilane $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS; 98%, Aldrich); $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{CH}_3\text{COO})_2$ (Aldrich); NH_4F (98%, Aldrich); methanol (abs., Aldrich) were used in the sol-gel syntheses.

Xerogel A of poly(3-mercaptopropyl)siloxane was prepared by mixing 21.4 cm³ (0.096 M) TEOS and 9.1 cm³ (0.048 M) MPTMS at $\sim 5^\circ\text{C}$. 1 g of $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{CH}_3\text{COO})_2$ was added as a catalyst. Afterwards, 4.75 cm³ (0.264 M) of water is added and after 5 minutes the stirring was stopped, and the solution was aged at room temperature. The formation of the gel was concluded after 80 days. The gel was separated and vacuum dried at 90°C for 6 h. Then it was washed by 1 L of water (pH of the last portion of filtrate was 7.0) and dried under the same condition again. The yield of the white product was 13.6 g.

Xerogel B of poly(3-mercaptopropyl)siloxane was prepared by stirring 0.053 g NH_4F (0.00144 M) in 4.75 cm³ of water and 20 cm³ MeOH, and 9.1 cm³ (0.048 M) MPTMS. 21.4 cm³ (0.096 M) TEOS was slowly added, while keeping the solution at $\sim 5^\circ\text{C}$. After less than 1 min the clear solution turned into an elastic gel, which was aged for 24 h. at room temperature. After washing and vacuum drying at 80°C , the yield of white powdery substance was 11.1 g.

Synthesis of xerogels with bifunctional surface layer. The organosilanes were added to 20 cm³ of methanol and 0.096 M TEOS, in the concentration described in Table 1. Afterwards, 4.75 cm³ (0.264 M) of water was added and the stirring was stopped. This gel formed after a few minutes, it was aged for 24 h. Subsequently, the gel was separated and vacuum dried at 90°C for 6 h. Then it was washed by 1 L of water and dried under the same condition again. The yields were respectively: 10.7 g for xerogel C, 11.8 g for xerogel D and 11.1g for xerogel E.

Element analysis of the obtained samples was executed in the Analytical laboratory of the Faculty of Chemistry of UMIST, U.K. Infrared measurements were performed on a Nicolet 5PC FT in the transmission mode. Samples were pressed into pellets using KBr. Thermogravimetric analyses were performed on a Perkin-Elmer at a heating rate of $5^\circ\text{C}/\text{min}$ in a flow of dry air. SEM pictures were taken on a JEOL Superprobe 733. Nitrogen adsorption-desorption isotherms were recorded on a Quantachrome Autosorb automated gas adsorption system. Samples were degasses at 120°C prior to the measurement. BET surface areas [7] and BJH pore size distributions [8] were calculated using commercial software.

Results and discussion

The synthesis of the xerogel A using $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{CH}_3\text{COO})_2$ as a catalyst is previously described by Parish *et al.* [9] and Maciel *et al.* [10, 11]. The synthesis of the xerogel B (poly(3-mercaptopropyl)siloxane) using fluoride ion as a catalyst has not been described earlier in literature.

The first method has a few unfavorable characteristics. Firstly, often the synthesis mixture forms two phases, which are sometimes hardly distinguishable. Secondly, the formation of the gel in the recipe for xerogel is very time-consuming (more than ten days). Thirdly, the use of $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{CH}_3\text{COO})_2$ as a catalyst results in non-porous xerogels (as can be inferred from Table 2). Fourthly, as it was shown in [10], the polysiloxane skeleton of the xerogel A does not have a dense cross-linking and has unhydrolyzed alkoxy groups.

These four points can be considered as serious disadvantages of the method with using of the $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{CH}_3\text{COO})_2$ catalyst. On the other hand, when fluoride ion is used as a catalyst, the synthesis of the xerogel proceeds very quickly: a clear, elastic gel is formed after less than 1 min. Also the other characteristics of xerogel B are superior as compared with the xerogel A.

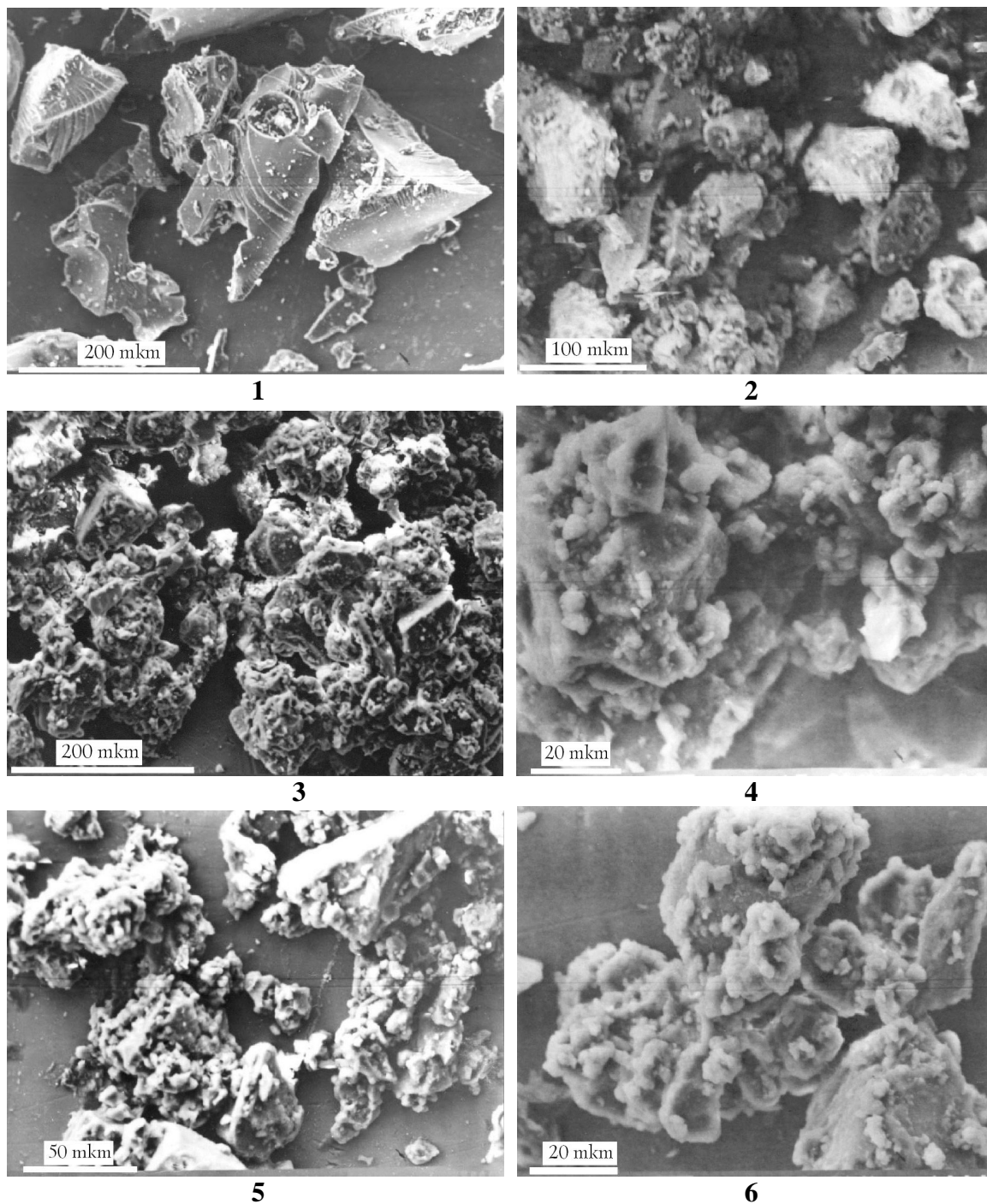


Fig. 1. SEM microphotos of xerogels obtained: 1 - sample A ($\times 200$); 2 - sample C ($\times 300$); 3 - sample D ($\times 500$); 4 - sample D ($\times 1000$); 5 - sample E ($\times 200$); 6 - sample E ($\times 1000$).

The proposed synthesis method has significant advantages in comparison with a method described by Voronkov's group for the grafting of polymercaptomethylsiloxane and polymercaptoethylsiloxane [12-14]. Authors [12-14] used single-component systems, which essentially narrow the opportunities of a flexible design on a surface and influence the structural-adsorptive characteristics of the formed xerogels. Moreover, Voronkov's approach can cause a partial decomposition of the functional groups.

Xerogels C, D and E were prepared without the addition of a catalyst [15], since the bifunctional aminosilanes create an autocatalytic effect. In other words, the amino group of the silane catalyses its own grafting to the surface, as it was described in [4]. Washing water pH value was the following: for the sample C in the beginning of washing – 8.4, in the end – 7.0; for a sample of D – 9.2 and 9.2 respectively; for the sample E – 9.8 and 10.2 respectively.

Fig. 1 shows the SEM microphotos of these 4 samples. Clear trends can be observed in these pictures. The xerogel A consists of irregular particles, frequently of triangular shape with sharp edges. The particle size is 150-200 μm . Looking at the samples C \rightarrow E microphotos an increasing connectivity between particles is observed: from 50-100 μm (C) up to agglomerates with the size 400 μm and more (E). Also, the content of aminopropyl groups grows from C to E. Therefore, we assume that the increasing number of amino groups and therefore the increasing pH during the synthesis results in a higher solubility of the silica matrix resulting in smoother particles bound together.

In Table 1 the results of the element analysis are summarized. These results show clearly that the obtained products have approximately the same concentration of functional groups that the primary synthesis mixture. So, for the sample C it makes 3.47 (in an original mixture - 3.0), for D - 1.12 (1.0) and for E - 0.36 (0.33).

Table 1. Composition of obtained xerogels and contents of functional groups.

Sample	Molar ratio of TEOS/MPTMS/ APTES	Element analysis data, in wt. %					$^1\text{C}_{\text{NH}_2}$ mmol/g	$^2\text{C}_{\text{NH}_2}$ mmol/g	C_{SH} mmol/g
		C	H	N	S	Si			
A	2 / 1 / 0	12.8	4.0	-	10.4	29.8	-	-	4.00
B	2 / 1 / 0	15.5	3.0	-	12.6	28.4	-	-	4.50
C	2 / 0.75 / 0.25	15.0	3.4	1.4	9.1	31.9	0.95	0.77	3.30
D	2 / 0.5 / 0.5	14.6	3.4	2.6	6.2	32.5	1.80	1.54	2.14
E	2 / 0.25 / 0.75	14.6	3.4	4.0	2.9	32.8	2.80	2.86	1.00

¹ from the data of the element analysis on nitrogen

² from the data of acid-base titration

It also shows that the mercaptopropyl functional groups is less susceptible to washing procedures (more strongly bound) as compared with aminopropyl groups. Besides, acid-base titration proved that all amino functions are active and available on the surface, irrespective of ratio MPTMS/APTES during synthesis. The IR spectra of the materials are presented in Fig. 2.

For all sample, strong absorption in the 1000-1200 cm^{-1} region is observed and assigned to three-dimensional skeleton of siloxane bonds [16]. The presence of propyl chains is obvious from set of bands of a weak intensity in 1300-1500 cm^{-1} region and two (sometimes - three) bands of medium intensity in 2800-3000 cm^{-1} region. The latter bands are

assigned to stretching vibrations $\nu_{s,as}(\text{CH})$. In the IR spectrum of the xerogel A (Fig. 2, A) shows a low-intensity absorption band at 2565 cm^{-1} , assigned to $\nu(\text{SH})$.

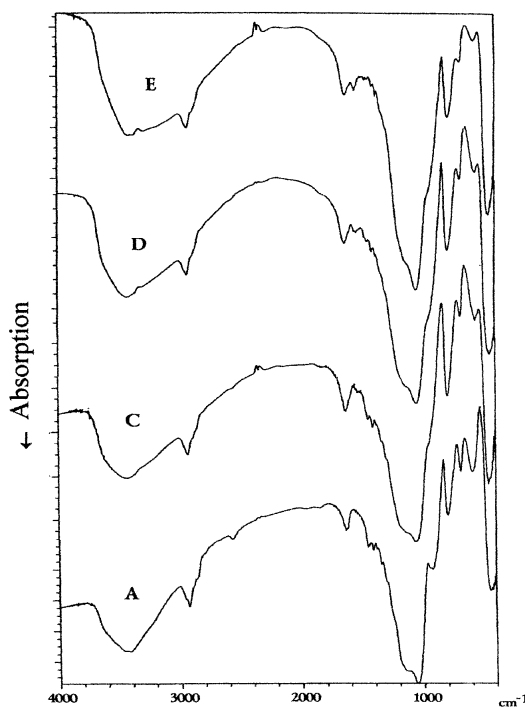


Fig. 2. IR spectra of xerogels A, C, D, and E.

Upon reducing the of MPTMS concentration in the synthesis mixture, its intensity decreases to almost absent in the IR spectrum of xerogel E (Fig. 2, E). All substances contain water, as can be seen from the $\delta(\text{H}_2\text{O})$ vibrations at $1600\text{-}1650\text{ cm}^{-1}$ and the broad band about 3000 cm^{-1} of $\nu(\text{OH})$ of the adsorbed water. Samples of D and E (Fig. 2, D and E) show slight absorption at ~ 3300 and $\sim 3375\text{ cm}^{-1}$; which can be assigned to the symmetric and asymmetric stretching vibrations of N-H in the amino groups. These bands are absent in the IR spectrum of the xerogel A. The weak band at 1560 cm^{-1} in samples D and E becomes more intense as a function of the loading of amino groups and is assigned to the $\delta(\text{RNH}_3^+)$ of the alkylammonium cations, which are formed on the surface of polyaminosiloxanes [17].

The thermo-analytical curves for the synthesized xerogels are given in Fig. 3 and 4. The small weight losses at 100°C (A - 2.6%; B- 1.1%; C - 3.1%; D - 4.4%; E - 5.3%) is assigned to the desorption of water. For the xerogel B the weak exothermal band at 280°C is more pronounced than for the xerogel A (see Fig. 3). The intensive burning out of surface layer for the sample B would begin at 250°C , while for A - at 265°C . Though the total weight losses for both samples are very similar (for A -27.2%; for B- 26.5%), two exothermal effects are observed for sample A above 500°C . It is possible that the reason of these differences is the presence of porosity in the sample causing the large availability of function groups. Besides, for the synthesis of the xerogel A, $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{CH}_3\text{COO})_2$ was used as a catalyst. Moessbauer spectroscopy [18] has shown that this molecule remains incorporated/adsorbed on the final gel. Sample E contains the least amount of mercapto groups. The thermograms of samples C and D (Fig. 4, C and D) have only one strong exothermal effect at 350°C .

Thus, the surface layer of the xerogels with a ratios of functional groups SH/NH₂ 3:1 and 2:2 are the most thermally steady. Poly(3-aminopropyl)siloxane, obtained at the ratio

TEOS/APTES 2:1, has one exothermal peak at 270°C [19]. Thus, it is possible to assume an effect of synergism in the C and D samples.

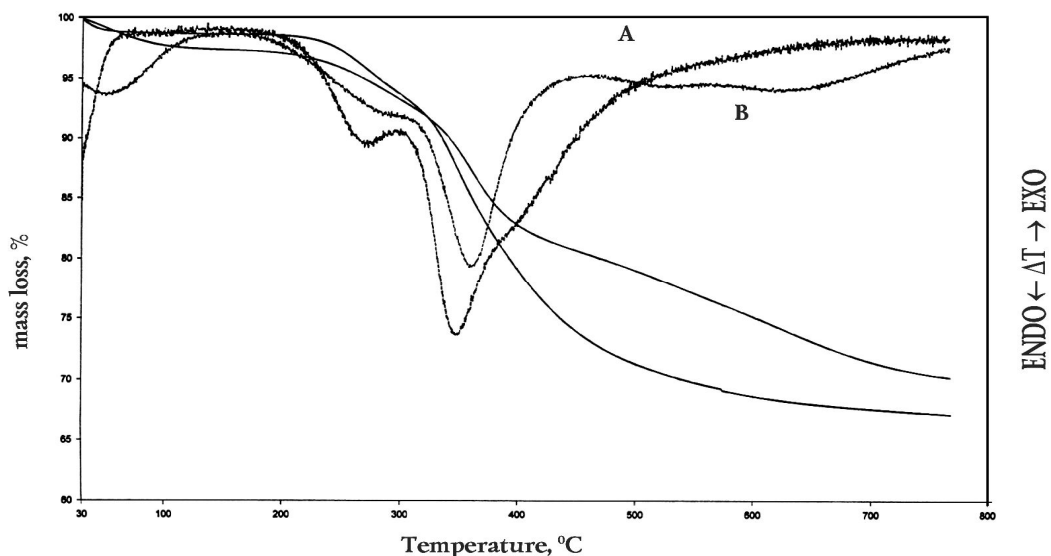


Fig. 3. Thermoanalytical curves for xerogels A and B.

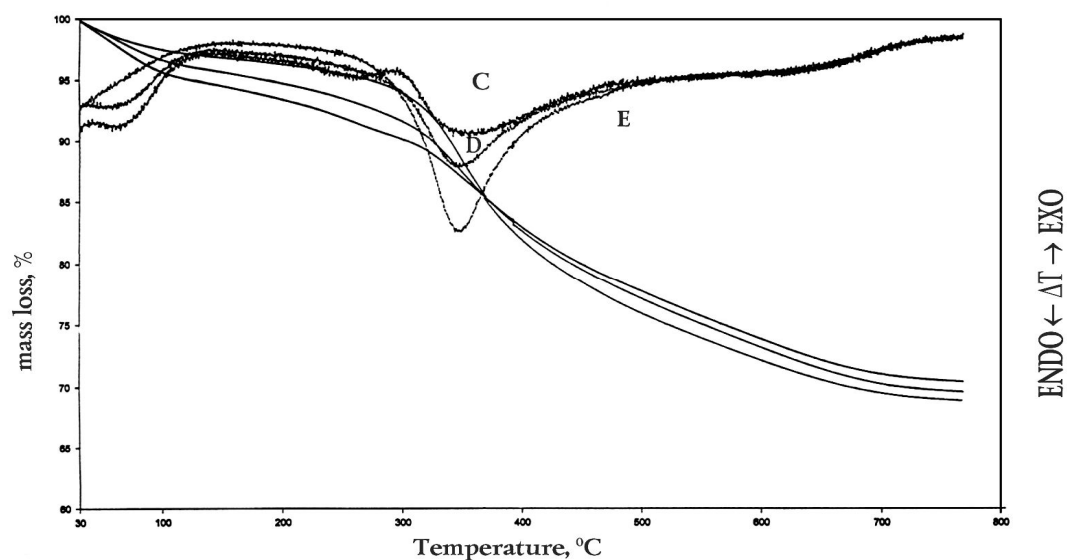


Fig. 4. Thermoanalytical curves for xerogels C, D and E.

The structure-adsorption characteristics of the xerogels obtained are represented in Table 2. Sample A, prepared by an use of the Sn-catalyst, is not porous at all. Polymercaptomethylsiloxane, synthesized in an alkaline conditions (of single-component system) [12], has a specific surface area of 80 m²/g (on *n*-hexane) and 162 m²/g (on argon). The xerogels C, D and E, containing bifunctional surface layer, have very high surface areas

and pore volumes (see Table 2). All samples with bifunctional surface layer have a capillary-condensation hysteresis (Fig. 5), pointing to the presence of mesopores.

Table 2. Structure-adsorption characteristics of synthesized samples.

Sample	S_{sp} , m^2/g	V_s , cm^3/g	d_{eff} , nm
A	< 1	-	-
B	216	0.152	2.8
C	214	0.358	6.7
D	217	0.302	5.6
E	234	0.675	11.5

It is interesting to note that for the xerogel E, containing the smallest amount of amino groups, the hysteresis curve is broader and shifted to larger relative pressures (see Fig. 5). The average pore size is nearly twice as large as that for the samples C and D (Table 2), and is very close to the pore size for polyaminosiloxanes, obtained in the same conditions [19]. Also, the surface areas slightly increase from sample C to E, and thus S_{sp} values grow from 214 up to 234 m^2/g with an increasing of amino groups contents (Table 2).

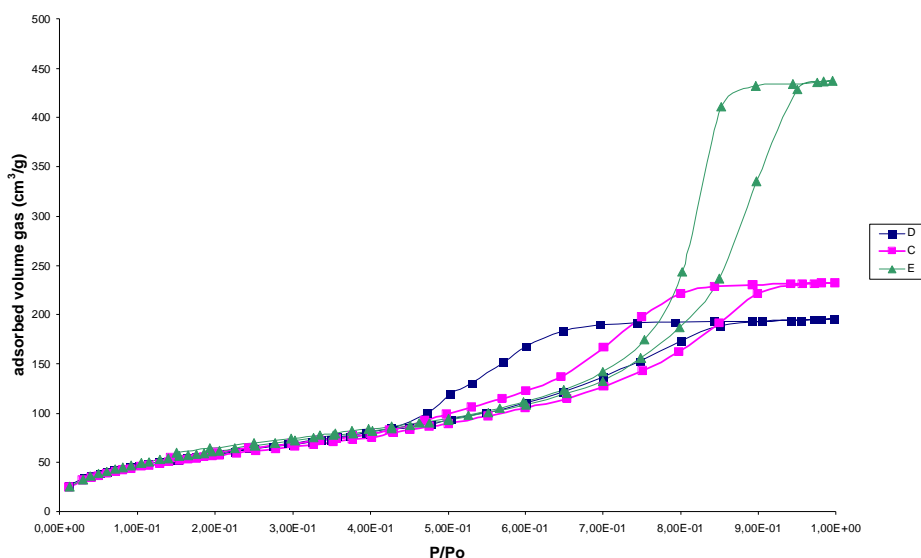


Fig. 5. Isotherms of nitrogen adsorption for the samples C, D and E.

The pore size distributions for the samples are shown in Fig. 6. For the sample B with a monofunctional surface layer this distribution is very narrow and the average pore size lies at the boundary between micro- and mesopores (see Table 2). With an introduction into surface layer of aminopropyl groups (sample C), a biporous structure occurs with two different types of mesopores. At higher contents of amino groups (sample D, Fig. 6) the biporous structure is still maintained. However, for the sample with the maximum content of amino groups in surface layer (Fig. 6, E), a monoporous system with large mesopores is observed again. It is interesting to note that in samples C and D, containing bifunctional surface layer, the effective diameter of the smallest mesopores is close to the mesopores of a

sample, containing only mercaptopropyl groups. Therefore, we must conclude that in those intermediate cases, there is no simple correlation between the composition of the initial gel and the composition and structural- adsorptive properties of the final xerogels

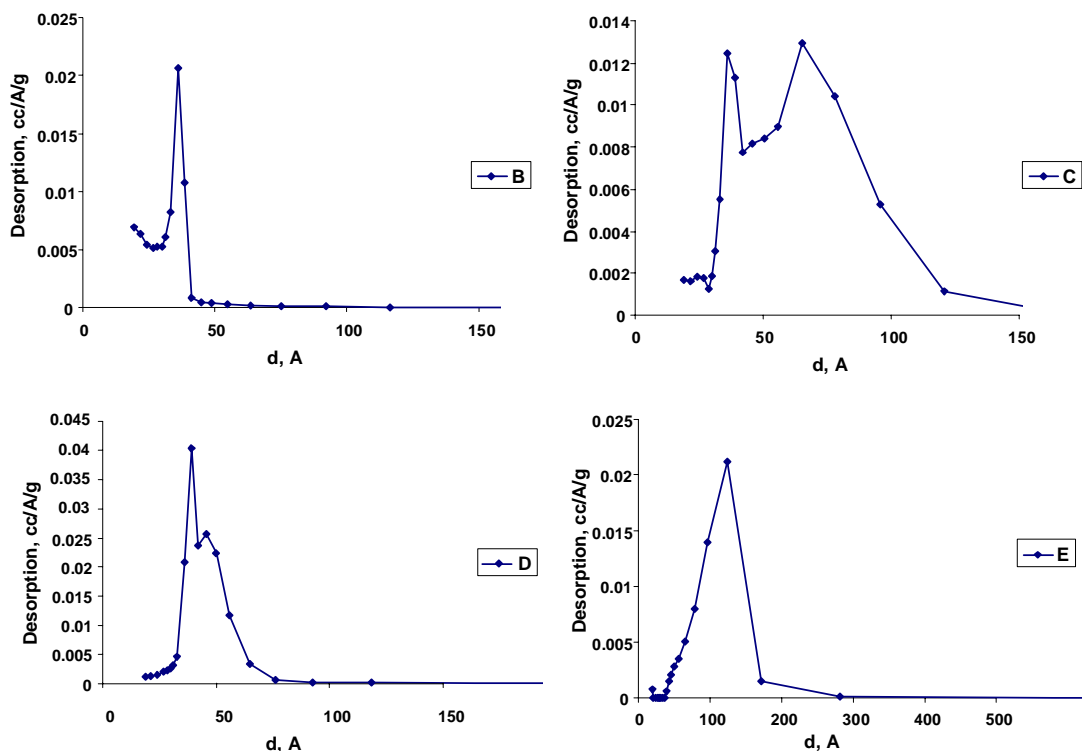


Fig. 6. Pore size distributions for the samples B, C, D, and E.

Conclusion

Polyorganosiloxanes with bifunctional surface layers have been synthesized in one-stage synthesis method. It is shown that the relative concentration of both functional groups can be varied in a wide range (SH/NH₂ ratios were 4:0; 3:1; 2:2; and 1:3). Such bifunctional xerogels have a high potential for the selective adsorption of various metal ions in aqueous media. Synthesized xerogels have high specific surface areas and pore volumes. All obtained materials are mesoporous.

Acknowledgement

PVDV acknowledges the FWO-Vlaanderen for the financial support.

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