CHARACTERIZATION OF SILICA SORBENTS BY SANS

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Silica sorbents were prepared and investigated by small-angle neutron scattering (SANS). The surface area, pore volume, mean pore diameter and thickness of the pore walls determined by traditional adsorption technique are compared with the mean radius or correlation length determined by SANS method. The pore size determined by adsorption methods is far from the values of the scattering object size obtained by SANS method. It is supposed that the scattering objects in SANS are not pores but the walls of the pores.

Keywords: Silica sorbents, Pore size, Small-angle neutron scattering

INTRODUCTION

Silica gels under study are materials intended for the use as packing sorbents in liquid chromatography (LC), particularly in gel permeation chromatography (GPC). The quality of silica for LC should meet strict physical and chemical parameters. One of these parameters is their pore size. Especially in GPC it is very important to know this parameter because it controls the whole process of chromatographic separation.

The pore size and thickness of pore walls can be measured by various methods. Most common is the mercury intrusion technique, which unfortunately has some limitations, mainly in the range of very narrow pores. The mean pore diameter of silica can also be evaluated from its pore volume knowing the surface area of the material.

SANS technique is a nondestructive method providing average information about a large number of scattering objects [1], in our case about objects (pores or walls) in silica. Better knowledge about pore size and thickness of the wall and their distribution can contribute to the improvement of the sorbent properties.

EXPERIMENTAL

For SANS measurement we used five silica samples (designated N2, N5, N18, N28, N300) of different pore size. Samples were 1 mm thick.

Preparation of silica gel samples:

N2: Dilute nitric acid was added to diluted sodium water glass, gelled material was dried at 110°C, then washed out from all salts by distilled water and again dried.

N5: A sol of silicic acid was mixed with a solution of ammonium carbonate and resulting hydrogel of silicic acid was dried.

N18: Diluted sodium water glass was gelled by dilute solution of sulphuric acid. The hydrogel formed was treated with hot concentrated sulphuric acid, then washed out by water and finally the water displaced by ethyl alcohol, dried and then silica gel was heated at 700°C.

N28: Commercial silica gel, received from Tessek Company (initial surface area 420 m^2g^{-1}), was treated by boiling in saturated solution of NaCl. The material was than washed out from salts and dried.

N300: Commercial silica gel was calcined in mixture of inorganic salts. After cooling the material was washed out from salts and dried.

The SANS measurement were performed at the device V4 of HMI Berlin at room temperature. Wavelength was 0.6 nm. Powder samples were measured in cuvettes for sample to detector distances 1, 4 and 16 m, respectively. The scattering data were corrected for background, transmission and detector efficiency and calibrated for absolute intensity referring to the incoherent scattering of pure water by standard HMI's programs.

RESULTS AND DISCUSSION

Surface area (*SA*) of silica gels was calculated from the measured adsorption isotherms of Ar at 77 K according to the method BET [2]. Pore volume (*PV*) was determined from the measured tapped bulk density (*BD*) according to formula:

$$PV = \frac{0.55}{BD} - SV$$

where *PV* is pore volume in $cm^3 \ g^{-1}$, *BD* is tapped bulk density in $g \ cm^{-3}$, *SV* is specific volume of silica (in our case it is 0.43 $cm^3 \ g^{-1}$) and 0.55 is parameter expressing mean interparticle volume fraction. The mean pore diameter, *D*, was then calculated as follows:

$$D = \frac{4PV}{SA}$$

Thickness of the pore wall for slit shaped pore (W_{slit}) and cylindrical pores (W_{cyl}), respectively were calculated as follows:

$$W_{slit} = \frac{2SV}{SA} \qquad\qquad W_{cyl} = \frac{SV}{SA}$$

Characteristics of our samples are presented in table 1.

Figure 1 presents the dependence of the scattering intensity on q-value in the logarithmic scale for the silica gel samples N2 and N5, respectively. Experimental points in the figure were obtained by data reduction. Underneath there is the solid line presenting fitting by polydisperse hard spheres model according to Pedersen [3], with added power-law term describing lower q part of the experimental points. Porod exponent for both samples was equal to 4 and mean radii for N2 and N5 were 2.2 and 5.7 Å, respectively.

Scattering curves of silica gel samples N18 and N28 are shown in figure 2. These experimental points could not be fitted with above model. The lower q part of these spectra already follows the power-law behaviour with the exponent equal to 4. These spectra
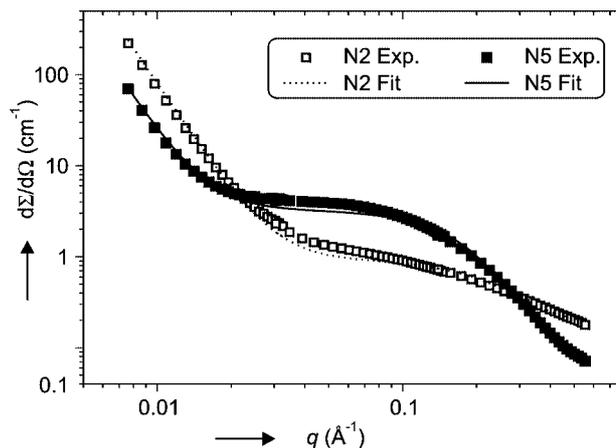
Figure 1. Scattering curve from silica gel samples N2(□) and N5(■). The rectangulars represent measured points, lines represent simulation by polydisperse hard sphere model.
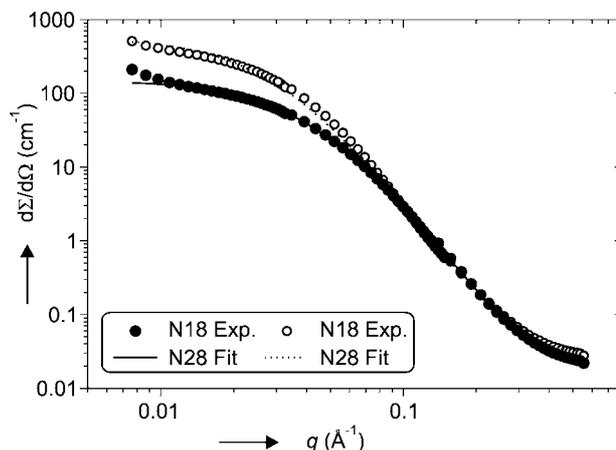
Figure 2. Scattering curve from silica gel samples N18(○) and N28(●). The circles represent measured points, lines represent simulation by fractal model.

were fitted with fractal model [4]. The power law behaviour with exponent 4 suggests that there is no fractal surface in the samples and it really gave Hausdorf dimensionality equal to 3.05. The correlation

Table 1. Characteristics of silica gel samples. Surface area (*SA*), Pore volume (*PV*), Mean pore diameter (*D*), Thickness of slit pore wall (W_{slit}), Thickness of cylindrical pore wall (W_{cyl}) and SANS results (SANS). The mean deviation, σ: for SA is σ = ±5%, and for PV is σ = ±10%.

Sample	SA ($m^2 \ g^{-1}$)	PV ($cm^3 \ g^{-1}$)	D (Å)	Wslit (Å)	Wcyl. (Å)	SANS (Å)
N2	820	0.4	20	10	5	2.2
N5	600	0.65	50	14.3	7.2	5.7
N18	420	1.9	180	20.5	10.2	24
N28	136	1.0	280	63	31.5	34
N300	13	1.3	3000	661	330	>300

length was determined to be 24 and 34 Å for samples N18 and N28, respectively.

Figure 3 shows the scattering curve for the last silica gel sample N300, which exhibits the power-law behaviour in the whole q-range. The size of the scattering objects estimated to be more than 300 Å is too large to be reflected by the scattering curve. The exponent being equal to 4.38 for whole q-range, reveals fuzzy surface as was found in silica samples prepared by other method [5]. All results are summarised in table 1.
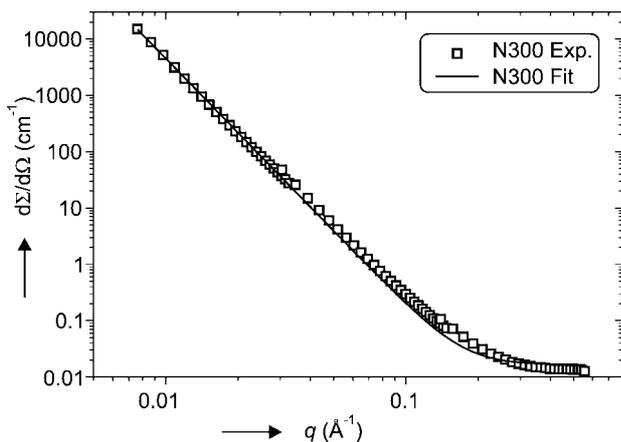
Figure 3. Scattering curve from silica gel sample N300(□). The rectangulars represent measured points, solid line represents simulation by power law model.

CONCLUSION

The pore size determined by the adsorption method is far from the values measured by the SANS method. It is clear that formally it is impossible to distinguish whether the scattering objects are pores or walls. The evaluation of our results seems to reveal that objects of scattering are not the pores themselves but the walls of these pores. In this respect it would be also concluded that the walls seem to be more or less cylindrically shaped. Discrepancies in W_{cyl} and SANS for samples N2

and N5 respectively, are not so large if we consider a diversity of methods used for the calculation.

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CHARAKTERIZACIA SILIKAGÉLOVÝCH SORBENTOV METÓDOU
MALOUHLOVÉHO NEUTRÓNOVÉHO ROZPTYLU

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Pripravené silikagélové sorbenty sa sledovali malo-uhlovým neutrónovým rozptylom [SANS]. Merný povrch, objem pórov, stredný priemer a hrúbka stien pórov, stanovené klasickými adsorpčnými metódami sú porovnané so stredným polomerom alebo korelačnou dĺžkou stanovenou SANS metódou. Veĺkosť pórov stanovená z adsopčných merani nesúhlasí s hodnotami meranými SANS metódou. Následne sa predpokladá, že rozptylujúce objekty nie sú samotné póry, ale steny týchto pórov.