SPECTROSCOPY
OF AMBIENT MEDIUM

Estimation of Silica Material Pore Sizes from IR Spectra of Adsorbed Water

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Abstract—A technique for estimating the diameter of nanosize pores has been developed. It consists in filling a substance with liquid water, recording the absorption spectra of the substance with water, compiling a database of spectroscopic data which characterized the substance with different pore sizes, and retrieving the pore diameter of an arbitrary substance using an algorithm based on the regression analysis. The technique has been tested on silica samples of different porosity.

INTRODUCTION

The practical application of nanomaterials with different structural and physicochemical characteristics in modern technologies, medicine, and atmospheric aerosol research requires understanding the processes of interaction of a molecule with nanopore walls and diagnosing the structural properties of porous materials [1, 2]. The pore structure is diagnozed with different techniques, for example, electron microscopy, diffraction methods, and gas adsorption porosimetry [3].

The main technique used for determining the adsorption capacity of solids (for example, [4]) consists in estimation of the specific surface area of disperse and porous materials by the dynamic method of thermal desorption of adsorbate gases (nitrogen or argon) from a flow of a mixture of adsorbate with helium at a temperature of 77 K. A stationary flow of a mixture of helium with adsorbate in a constant composition is produced; a surface is "trained" by heating to temperatures of 350−700 K; then, the adsorbate is adsorbed from the flow of the mixture at a temperature of 77 K and again desorbed into the flow of the mixture by heating to temperatures of 200−300 K, and the concentration of the adsorbate in the mixture flow is measured. This technique makes it possible to determine the specific surface area based on the properties of physical sorption without taking into account the effect of chemical sorption. When high nitrogen concentrations are used, the thermal conductivity sensitivity of a detector drops sharply; therefore, the accuracy of the results decreases. In addition, the technique requires a sufficiently long time for measurements.

In [5, 6], a technique was suggested for pore size diagnostics based on the effect of the broadening of spectral absorption lines of gases in pores. The high-resolution spectrum of water in an aerogel shows the profile of rotational-vibrational line of water molecules to be significantly broadened due to collisions of the molecules with the pore walls in comparison with the halfwidth of absorption lines of free molecules. In [7], a technique is suggested for determining the parameters of the porous structure of a substance from high-resolution absorption spectra of water, which requires expensive equipment. To record high-resolution spectra of molecules in the gaseous phase, a long time and a long optical path in the absorbing medium are required; therefore, this technique can only be used to determine the parameters of relatively extended and transparent media such as aerogels.

As is shown [8, 9], the structure of the water absorption spectrum strongly depends on the volume where water is located. Studies of Raman and IR spectra of water in nanoporous samples of Gelsil [10], SiO_2 [8, 12], and in zeolites NaA [11] also have shown that intramolecular OH stretching vibrations are an informational sign of intermolecular H-bonding for water confined in nanomedia. In this regard, it is interesting to study the possibility of determining the parameters
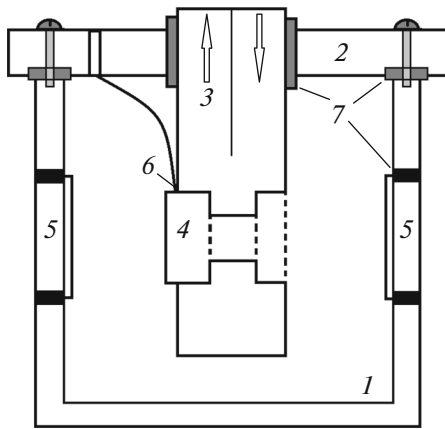
Fig. 1. Layout of the vacuum cell for recording the absorption spectra of water in silica: external vacuum casing (*1*); cover (*2*); brass holder with tubes for coolant supply and circulation (*3*); sample (*4*); windows of the vacuum casing (*5*); temperature sensor (*6*); heat-resistant gaskets (*7*).

of the porous structure of a sample from the absorption spectra of water adsorbed in the sample.

In this work, we studied the absorption spectra of water in nanoporous hydrophilic materials with the aim of developing a technique for determining the pore size from the water absorption spectra.

EXPERIMENTAL

The absorption spectra of water in porous materials were recorded at Bruker IFS 125M and Simex FT-801 Fourier spectrometers using a vacuum cell (Fig. 1). The spectral resolution was 2 cm^{-1}. The sample temperature was kept constant, $T = 296 \pm 0.5$ K, during recording.

The cell provides the possibility of thermal stabilization by pumping liquid through external aluminum vacuum case *1*. Brass holder *3* with isolated test sample *4* is inserted into the body of the vacuum casing. A coolant flows through the holder. Sample temperature is measured with thermocouple probe *6* with (graduation 0.1°) fixed on the holder on cover *2*. The cell is equipped with quartz windows *5* reinforced with heat-resistant gaskets *7*. The cell was preliminarily evacuated.

The experiment was carried out with three samples based on purified siliceous diatom flaps *Synedra acus*:

original valves (*S. acus*) and flaps etched with alkaline solutions (SAC30M and Ssp2t8). A sample of commercial Panreac silica gel (lot 174275.1211, particle size 63−200 μm) was also used. The pore sizes of the samples, determined by the method of low-temperature adsorption of nitrogen (SORBTOMETR-M device, Katakon JSC) are given in Table 1.

Before the start of the experiment, the powder of a sample under study was pressed into tablets with a diameter of 7 mm and a thickness of 2−4 mm. Several pellets were made of each material for further research. The hand press pressure ranged from 400 to 500 kg/cm^2, which did not violate the porous structure of the powder. Each sample was evacuated for an hour, after which the test substance was filled with water. To fill the pores with water, a pellet was kept on a damp cloth for 12 hours at a temperature of ~40°C.

The absorption spectrum of liquid water has broad bands in the regions near 5400 and 7000 cm^{-1}. To record the spectra, an absorbing layer 2−4 mm thick is sufficient, at which the absorption saturation threshold is not reached. The spectra measured for different pellets of one material agree with each other within 2−5%.

WATER ABSORPTION SPECTRA IN NANOPORES

Earlier, in [8, 13], we have shown that the region of the second triad ($\nu + \delta$) is more informative for studying the water spectra in nanoporous materials than the region of pure stretching vibrations 3000 cm^{-1} because the difference between the centers of the water absorption bands attains 100 cm^{-1} in this spectral range with variations in the pore diameter. In this work, the absorption spectra of water confined in nanopores of silicon nanoporous materials were recorded in the range 4000−9000 cm^{-1} with a spectral resolution of 2 cm^{-1}. This area contains the second triad ($\nu + \delta$) and the first hexad (2ν) of vibrational transitions of the water molecule.

Figure 2 shows the spectrum of a SAC30M sample (*1*). The spectrum contains an absorption band of the pellet material (4500 cm^{-1}) and absorption bands of liquid water (5200 and 6900 cm^{-1}), as well as a line structure associated with the absorption of atmospheric water vapor inside the Fourier spectrometer. The air temperature and humidity in the room was sta-

Table 1. Structural and texture parameters of the materials used

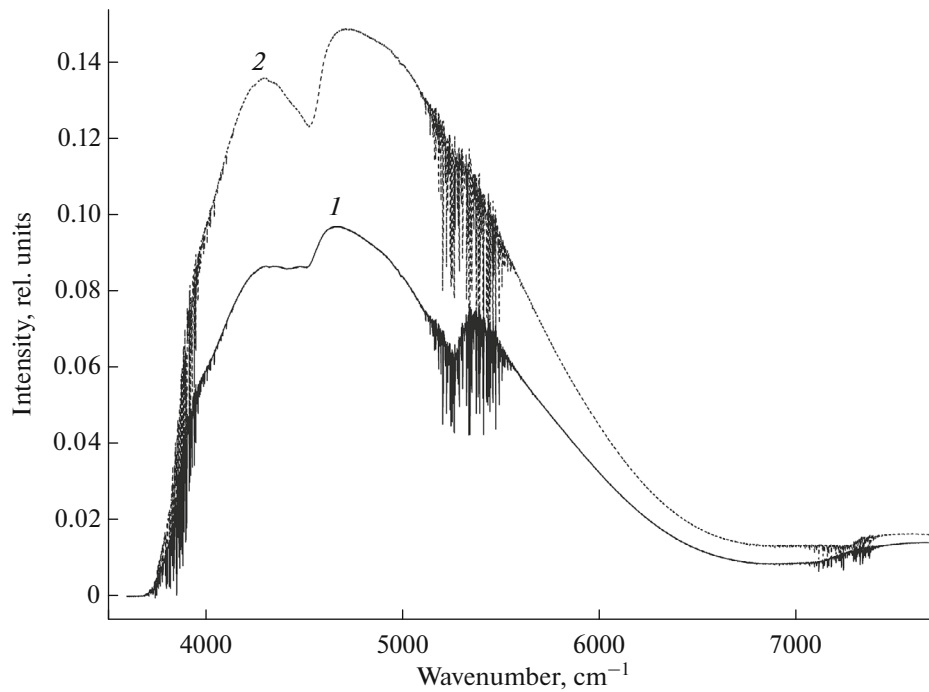| Sample	Specific pore surface, m^2/g	Specific pore volume, m^3/g	Pore diameter, nm
S. acus	10	0.015	9
S.A.C30M	14.6	0.015	6.15
Panreac	536.8	1.24	13.8
Ssp2t8	34.5	0.058	10.05

Fig. 2. Spectrum of the SAC30M sample before (*1*) and after (*2*) evacuation.

bilized with a Midea MSE-24HR air conditioner. Due to this, the use of spectrum (*2*) of a fully evacuated sample as the baseline allowed compensating the line structure.

Figure 3 shows the normalized absorption spectra of liquid water and water in pores in the range 4200–7500 cm^{-1}. The water absorption in the region 5200 cm^{-1} is twice as high as the absorption in the region 7000 cm^{-1}. Liquid water absorption band profile (*1*) significantly differs from profiles of the absorption bands of water confined in the pores (*2–5*) in shape, position of the center, and halfwidth. The bandwidth of water confined in the pore volume attains ∼600 cm^{-1} in the region 5200 cm^{-1} and up to ∼1000 cm^{-1} in the region 7000 cm^{-1} for different samples; the shift of the maxima of the water absorption bands attains 50 cm^{-1} near 5200 cm^{-1} and up to 150 cm^{-1} near 7000 cm^{-1}. Thus, the variability of the profile with the pore diameter is most pronounced in the region of the second triad.

To interpret the variations in the profile, it was divided into components with the use of different models; the physical essence of the components is attributed to different configurations of molecules due to both the wall interaction and different degrees of molecular clustering of water inside nanopores [14, 15].

The main idea of this work is to consider the spectra recorded from the point of view of regression analysis of the profile as a whole. The dependent parameter in the analysis is the pore diameter of a particular material, and the independent parameter is the array of equidistant points in the water absorption band in the pores of this material.

REGRESSION ANALYSIS OF THE SPECTRUM

Let us have M spectra in a certain fixed frequency range in the form of the absorption coefficients at N points uniformly distributed over this range:

$$\begin{aligned}
&\left\{K_1^1, K_2^1, \ldots, K_N^1\right\}, \\
&\left\{K_1^2, K_2^2, \ldots, K_N^2\right\}, \\
&\qquad \cdots \\
&\left\{K_1^M, K_2^M, \ldots, K_N^M\right\}.
\end{aligned} \quad (1)$$

Let the set of L parameters be known for each of these M spectra:

$$\begin{aligned}
&\left\{S_1^1, S_2^1, \ldots, S_L^1\right\}, \\
&\left\{S_1^2, S_2^2, \ldots, S_L^2\right\}, \\
&\qquad \cdots \\
&\left\{S_1^M, S_2^M, \ldots, S_L^M\right\}.
\end{aligned} \quad (2)$$

In our case, the parameter is the pore sizes ($L = 1$).

The task is to obtain a prediction spectrum for water in a substance with a given pore size. To do this, we need to create a model for each point of the desired spectrum based on data (1) and (2). This model can take the form of a linear function of the given parameters S_j^*:

$$K^i = A_0^i + \sum_{j=1,L} S_j^* A_j^i, \quad i = \overline{1,N}, \qquad (3)$$

where model parameters $A_0^i, A_1^i, A_2^i, \ldots A_L^i$ for each point of the spectrum are determined from fitting by the least-squares method:

$$\sum_{m=1,M} \left[\left\{ A_0^i + \sum_{j=1,L} S_j^m A_j^i \right\} - K_i^m \right]^2 \Rightarrow \min_{A_0^i, A_1^i, \ldots, A_L^i}, \qquad (4)$$

$i = \overline{1,N}$ is the number of a spectral point.

Then, the spectrum at a desired point with the required pore parameters can be predicted using expression (3).

The inverse problem is to retrieve the parameters S_j^* (the nanopore diameter in our case) from the known spectrum K_i^*, $i = \overline{1,N}$, of a mixture. Then, the standard deviation of the model from the known spectrum with respect to the parameters S_j^* is minimized simultaneously at all spectrum points :

$$\sum_{i=1,N} \left[\left\{ A_0^i + \sum_{j=1,L} S_j^* A_j^i \right\} - K_i^* \right]^2 \Rightarrow \min_{S_j^* \, j=1,L}. \qquad (5)$$

We have created a program where we analyze the input data and form a database of spectra with the same range and the number of points. The same number of frequency points for all spectra is ensured by the interpolation procedure. Then, a model has been constructed for each point of a desired spectrum based on data (1) and (2).

ESTIMATION OF PORE SIZE

The pore size of a material was estimated from the spectrum of water contained in the pores with the use of regression analysis. The pore diameters of three of the four (reference) samples were introduced as known parameters. The absorption spectra of water in the reference samples were used to construct linear regression model (5), connecting the pore diameters with the absorption coefficients at the points of a spectrum. The pore diameters of the fourth (conventionally unknown) sample were determined from the recorded spectrum by minimizing Eq. (5).

Table 2 shows the values of the pore diameter D derived from the percentage of water at the pore centers for different rated pore diameters D_0. All four samples were used as an unknown sample in turn. The error corresponds to the spread of values derived from the analysis of several spectra of one sample.

Table 2 shows that the technique suggested for estimation of the pore diameters gives good results. The pore diameters found coincide with the data obtained by the gas adsorption method within the measurement
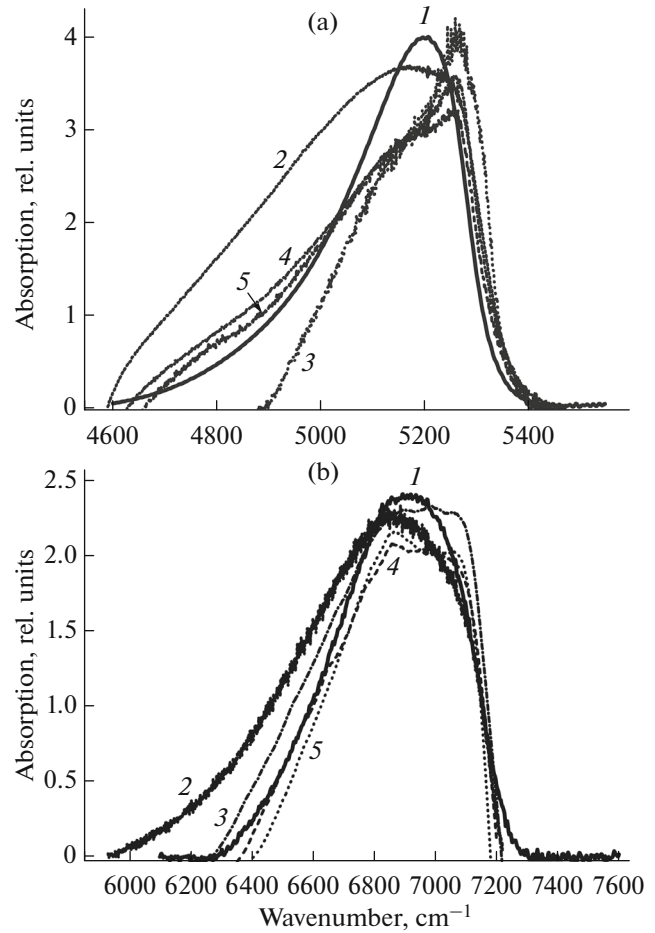

Fig. 3. Absorption spectra of liquid water confined in nanopores of different diameters in the absorption band (a) $\nu + \delta$ and (b) 2ν: liquid water (*1*); *S. acus*; Panreac (*3*); SAC30M (*4*); Ssp2t8 (*5*).

error. The technique does not require the use of liquid nitrogen and is quite fast, measurements take only a few minutes. A concept of a statistical pore size distribution for any, even calibrated, nanoporous material should be noted. The technique suggested allows one to calculate the average pore size in a sample.

CONCLUSIONS

Based on the regression analysis of the absorption spectrum of water confined in nanopores of silica

Table 2. Pore diameters of the samples under study

Sample	D_0, nm	D, nm
Ssp2t8	10	9.8($\pm$0.5)
S. acus	9	8.9($\pm$0.7)
Panreac	13.8	14.0($\pm$0.5)
S.A.C30M	6.15	6.8($\pm$0.8)

Ssp2t8, *S. acus*, Panreac, and SAC30M, a technique for estimating the pore diameter has been developed. The porosimetry procedure consists in filling a substance with liquid water, recording the absorption spectra of the substance with water, compiling a spectroscopic database which characterizes substances with different pore sizes, and retrieving the pore diameter of an arbitrary substance by regression analysis. The error of the technique is less than 1 nm, and the analysis time is less than 10 min. The software has been developed to automate the porosimetry procedure.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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