ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 6, pp. 1008–1013. © Pleiades Publishing, Ltd., 2007.
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State of Water in Amorphous Silica Samples from Rice Hulls: a ^{1}H NMR Study

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Received April 25, 2006

Abstract — Behavior of molecules of adsorbed water in rice hulls, weevil, and amorphous samples of carbon-containing (carbonized, SiO_2 content 47%) and pure silica was studied by ^{1}H NMR spectroscopy in the temperature range from 200 to 298 K. The temperature dependence of the signal intensity from humid samples shows a decrease in temperature of freezing of the adsorbed water and presence of unfrozen water. This dependence was used for estimating the pore size distribution. For pure amorphous silica, the pore diameter is in the range from 50 to 150 Å with a maximum at about 85 Å.
DOI: 10.1134/S1070363207060096

Silicon oxides find wide application in the modern technology as supports for sorbents and catalysts, fillers for rubbers, and medicinal preparations. Among silicon oxides, silicon dioxide (silica) is used most widely, being a versatile chemical compound whose structural parameters (particle size, strength, specific surface area, pore volume and diameter, refractive index) can be varied in a wide range [1–3]. Silica is commonly produced from various kinds of mineral raw materials [4].

Nontraditional but promising sources of silicon dioxide are by-products from rice production: straw and hulls. These are renewable, cheap, and readily available raw materials with relatively stable chemical composition. Rice hulls are accumulated at plants for production of rice groats and contains 15 to 20 wt% amorphous silica. The methods for preparation of amorphous silica involving two-step oxidative firing of the plant material and some of its properties (composition and content of impurities, density, bulk weight, shape and size of particles, and range of specific surface area and pore diameter values) were described in [5–7]. It was found also that the biogenic silica obtained in a thermal process commonly contains 0.5 to 5% adsorbed water depending on the technology of the raw material pretreatment.

The structure of rice hulls have been described in details in [8]. The rice hulls consist of four layers containing silica. The highest content of silica is in the outer (first) layer (epidermis). Upon firing, rows of joined cones retaining their shape can be clearly seen on the hull surface (Fig. 1a). Along with silica forming the shell framework, the shell contains various organic compounds (cellulose, lignin, lipids, pentosans, etc.) whose removal results in the formation of voids (Fig. 1b). The silica particles formed by oxidative firing at 923 K are easily broken down; their size varies from 100 to 0.02 μm, and diameter of main pores and specific surface area depend on the technology of the palea treatment [7].

In a number of recent papers, the methods of differential of scanning calorimetry [9, 10] and ^{1}H NMR spin echo [11–15] were applied to studying the size distribution of the pores and examining the character of binding of water molecules on the surface and inside the pores in different silica gels.

The aim of this study was to examine the size distribution of the pores and features of hydrogen bonding in moistened samples of the initial rice hulls and in amorphous samples of carbonized and pure silica prepared from it, using the pulse method of broad band ^{1}H NMR spectroscopy at temperatures in the range from 200 to 298 K.

^{1}H NMR spectra of four samples examined previously by various physicochemical methods [6] were studied: dry samples, (*A*) rice hulls, (*B*) rice weevil from unripe rice, (*C*) black carbonized silica, and

(*D*) white amorphous silica; the respective moistened samples are marked with primes.

The ^{1}H NMR spectra of air-dry samples *A*–*D* contain broad asymmetric bands (half-width about 2500 Hz) with a chemical shift of about 5 ppm. Figures 2 and 3 show the ^{1}H NMR spectra of dry and moistened samples *A*, *A*' and *D*, *D*'. The spectrum of sample *D*, along with the broad band, contains a weak shoulder with a chemical shift of 0.65 ppm.

The ^{1}H NMR spectra of moistened samples *A*'–*D*' contain strong and narrower bands (half-width 800 to 1000 Hz) compared to the spectra of the corresponding dry samples; the water signals have a typical downfield "tail." The signal with a chemical shift of 0.65 ppm is absent in the spectrum of *D*'. The observed signals are assigned to the protons of Si–OH groups and water on the silica surface and in the pores, i.e., all the samples of both dry and moistened silica contain O–H protons in various environments.

According to [12], silica can contain at least six types of OH protons: the hydroxy groups of water molecules not involved to associates (I), protons of OH groups involved in H bonds of O–H···O–H··· (II) and H–O–H···O–Si (III) type, protons of silanol groups Si–OH (IV) and Si–O–H···O–H (V), and

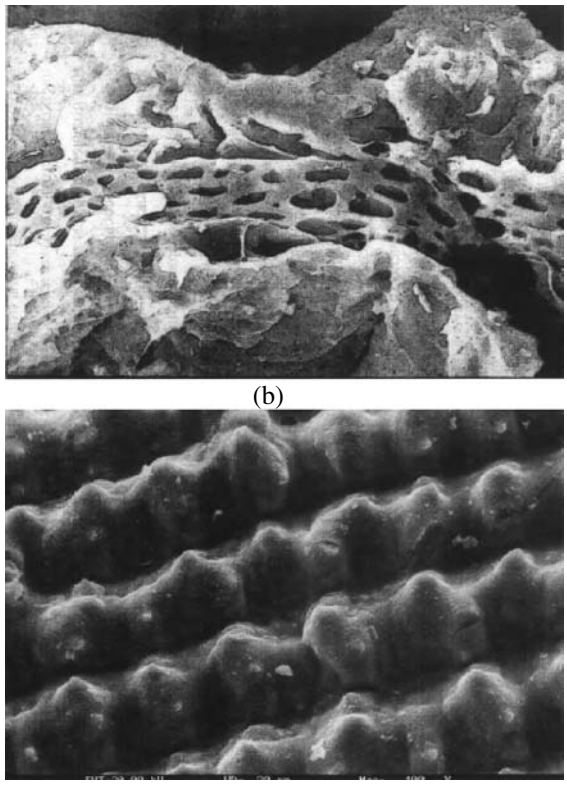

Fig. 1. Electron micrographs of (a) rice hull surface after thermal firing, magnification ×500, and (b) section of a particle of rice hull, magnification ×1000.

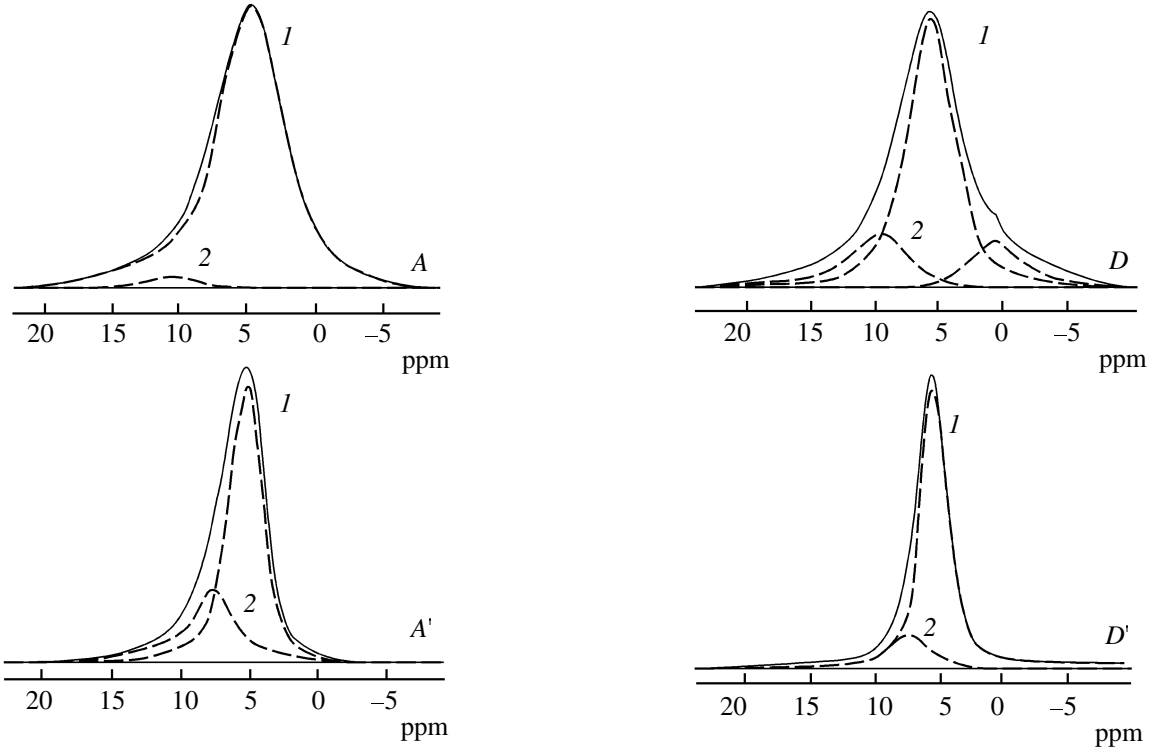

Fig. 2. ^{1}H NMR spectra of dry and moistened samples *A*, *A*', *D*, and *D*' and their resolution into components *1*–*3*.

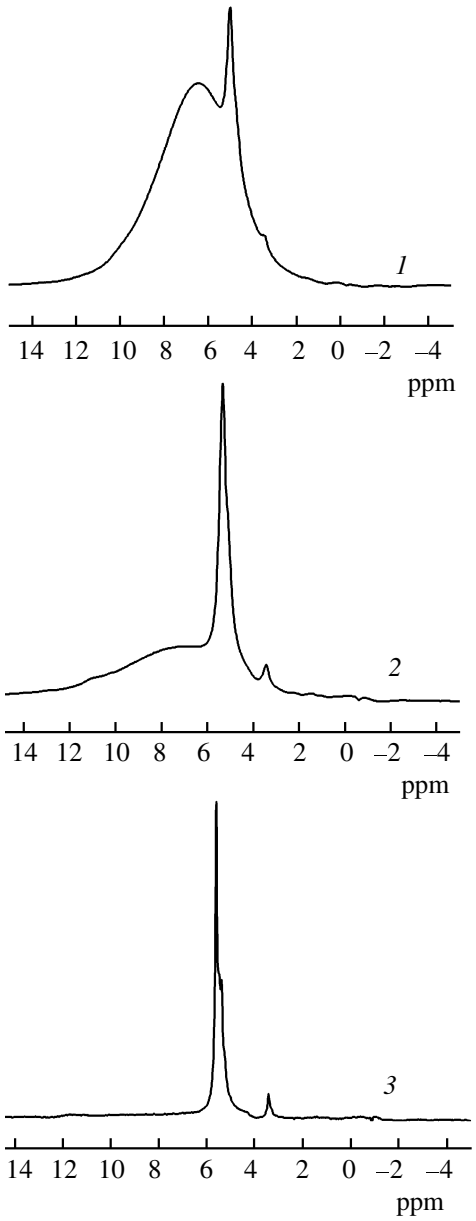

Fig. 3. ^{1}H NMR spectra of moistened sample *D*' at various temperatures: (*1*) 267 K, (*2*) 258 K, and (*3*) 225 K. Two peaks with chemical shifts of 4.2 and 3.47 ppm are the signals of OH and CH_3 residual protons in the deuteromethanol reference.

protons of water molecules involved in H bonds with the atoms of the siloxane groups Si–O–Si (VI).

H–O–H

One of the components (*1*) resolved by analysis of the shape of broad signals has a chemical shift of 4.5 ± 0.5 ppm for samples *A* (*A*') and *B* (*B*'), 6.0 ± 0.5 ppm for samples *C* and *D*, and 5.6 ppm for *C*' and *D*'. It is assigned to protons of water involved in an H bond of the O–H···O (II) type. This signal can be assigned not only to the protons of bulk water (whose content in the dry samples is low), but also to protons in the H bonds with silanol groups of types III and V. The second component (*2*) resolved from the broad band with a chemical shift of 8.5–9.5 ppm in dry and 7–8 ppm in wet samples corresponds to water protons bound with silica pores walls in mode V according to [12]. For sample *D*, the weak upfield shoulder (line *3*) with a chemical shift of 0.65 ppm can be most probably assigned to the protons of free Si–OH groups (IV). This signal is not observed in the spectrum of moistened sample *D*', probably because of fast exchange with the protons of bulk water.

Freezing of water is manifested in the ^{1}H NMR spectra by a decrease in the integral intensity (area) and broadening of the water proton signal. Comparison of the proton signals at different temperatures in the spectra of sample *D*' (Fig. 3) suggests a decrease in freezing temperature of the major fraction of water and existence of unfrozen water down to a temperature of 220 K.

Appearance of the unfrozen component is associated with changes in the water properties in the presence of any "surface" [14]. However, this "surface" (pore walls) interacts not with water directly, but only with the neighboring water molecules, which form layers connected with Si–OH and Si–O–Si groups. The observed decrease in the freezing temperature depends both on the size of the pores (surface/volume ratio) and on the surface chemical structure. These parameters, in particular, characterize the adsorption properties of silica. NMR is widely used today for studying the nature of water interaction with silica and measuring the pore size [13–15, 16–18].

The plots of the integral intensity (area) of water proton signals on cooling from room temperature to 200 K, followed by heating from 200 K, are shown in Fig. 4.

The sharpest decrease in the ^{1}H NMR peak area for samples *A*' and *B*' was observed in the temperature range 273–260 K, and for samples *C*' and *D*', at 268–260 K. The peak area is proportional to the number of protons responsible for the signal (in the absence of saturation), hence, the area (in arbitrary units)–temperature plots allow estimation of the ratio of the mobile and frozen water: at approximately 260 K for sample *A*', 0.55/0.45; for sample *B*', 0.62/0.38; for sample *C*', 0.80/0.20; and for sample *D*', 0.70/0.30. The difference in these values probably reflects the role of organic components in the palea of samples *A*' and *B*'. Further decrease in temperature leads to a

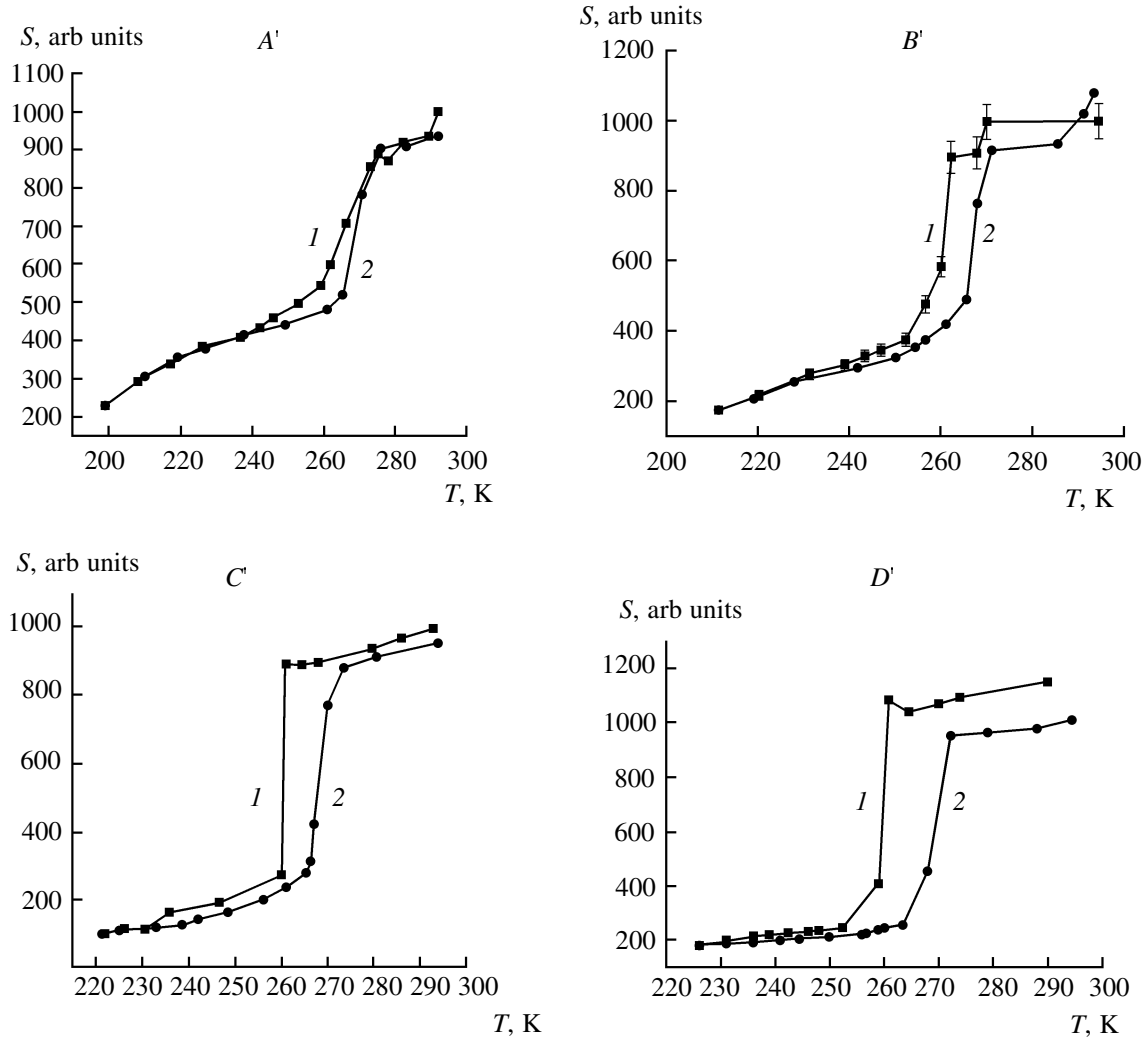

Fig. 4. Temperature dependence of the integral intensity of the ^{1}H NMR signals of samples *A*'–*D*', recorded in the course of (*1*) cooling and (*2*) heating.

stepwise decrease in the peak area, indicative of further freezing of motion of the residual water molecules. The heating of samples after their cooling initially leads to the similar smooth increase in the area of the signals of bound water (Fig. 4); the temperature dependences in the range 225–260 K (heating curves) for all the four samples practically coincide with those obtained in the course of cooling (cooling curves). Then the heating curves run below the cooling curves (hysteresis), and sharp change in the area of the ^{1}H NMR signal occurs at higher temperature than at cooling and in a narrower temperature range. The hysteresis is associated in part with the water sorption and desorption on cooling and heating in a closed volume. The shape of the hysteresis loop allows a conclusion that the pore type in the hull silica of samples *A*' and *B*' differs from that in amorphous silica samples *C*' and *D*', according to [1]. Organic inclusions in samples *A*' and *B*' can change both the size and shape of the pores. It was found previously [13] that the depression of the melting point of a liquid in pores obeys the Gibbs–Thomson law:

$$\Delta T_{melt} = K/d.$$

Here ΔT_{melt} is the melting point depression; *K*, coefficient specific for a given liquid (for water *K* = 583 Å ΔT_{melt}); and *d*, pore radius. The changes in the area of the water proton signals at temperature variations were used for estimating the pore diameter distribution in the samples of carbonized (*C*') and white amorphous (*D*') silica. The maxima of these distributions are at 85 and 90 Å, respectively, i.e., close to each other. However, in white silica (sample *D*'), the

distribution is broader (50–150 Å) than in carbonized silica (sample *C*', 70–130 Å).

Although the estimations thus obtained are approximate, they allow estimation of changes in the pore size on thermal treatment (firing) of rice hulls.

It is known that nuclear magnetic spin–lattice relaxation of protons is associated with the molecular mobility through magnetic field fluctuations. In the particular case of ordinary water, the proton spin-lattice relaxation time T_1 reflects both the mobility of a whole water molecule and motion of protons in X···H–O bonds. The initial water used in our experiments had the relaxation time at room temperature $T_1 = 2.83 \pm 0.15$ s.

The measured spin–lattice relaxation times T_1 of water protons in samples *A*–*B* and *A*'–*D*' at room temperature (for sample *D*', also at 261 and 236 K) are listed below.

Sample	$T_1 \times 10^3$, s room temperature	$T_1 \times 10^3$ s, 261 K	$T_1 \times 10^3$ s, 236 K
A	3.0		
B	8.4		
A'	10.02		
	5.0		
B'	9.3		
D'	3.75	5.5	3.5

As the broad signals of water differing in mobility mutually overlap, we measured the average relaxation time of the protons inducing this signal. The low T_1 values in dry samples show that the water mobility in them is very low. In moistened samples *A*'–*D*', T_1 increases by an order of magnitude, because they contain much more water and collisions of water molecules are more frequent. Lowering the temperature below the freezing point decreases T_1 also by an order of magnitude, and then it remains constant on cooling to 236 K. Closeness of T_1 values of the protons in dry samples at room temperature and in unfrozen water at low temperature means that T_1 at room temperature can characterize the mobility of water protons bound to the pore walls. This conclusion conforms to the data of previous papers on the supercooled state [19].

Thus, we showed that major changes in the intensity of ^{1}H NMR signal of water protons in the samples of rice hull, weevil, and biogenic silica occur in the region much below 273 K (on cooling the samples by 13–15°, on heating after freezing by approximately 5–7°C). The temperature dependence of the area of the ^{1}H NMR signal of water protons in the samples studied showed the presence of two types of water in them: mobile water and water whose protons are bound to protons and oxygen atoms on the silica pores walls. Estimation of the pore diameters and their size distribution by studying the study of temperature dependence of the intensity of the ^{1}H NMR signal of the water protons in carbonized and white silica gave values of 80 and 85 Å, respectively. The protons of water in the dry samples of rice hulls and in unripe weevil show low mobility ($T_1 \sim 10^{-3}$ s) at room temperature. The water protons in moistened samples are much more mobile at room temperature ($T_1 \sim 10^{-2}$ s). The mobility of the protons in the unfrozen fraction of water is close to that in dry samples.

EXPERIMENTAL

As the object of study we took plant by-products from a plant for production of rice groats in Krasnodar krai (taken in 2004), consisting of rice hulls, and also products of their processing. Sample *A* was rice hulls with a particle size of 2 mm and over, washed with water and dried in air; H_2O content 2.8%; sample *B* was rice weevil from unripe rice, contained in the hull waste in the amount depending on the agricultural technology; H_2O content 2.9%; sample *C* was carbonized silica obtained from sample *A* by firing at 723 K as in [6]; this product is black, with amorphous structure; content of H_2O 3.8, SiO_2 46.5%; sample *D* was amorphous silica prepared from sample *A* by two-tep oxidative firing, at 723 and 923 K, according to [6]. This product is white, content of H_2O 2.2, SiO_2 97.4%. To prepare moistened samples *A*'–*D*', samples *A*–*D* were poured over with hot (373 K) water, kept in water for 1 h, and then dried in air using filter paper. The line shape in the ^{1}H NMR spectra of all the samples (initial *A*–*D* and moistened *A*'–*D*') was recorded on an AMX-400 instrument without stabilization of the magnetic field in 5-mm ampules. The spectra at varied temperature were obtained on a WM-250 spectrometer. The samples were placed in 8-mm ampules, which were closed with special hermetic stoppers and then were placed in 10-mm NMR ampules containing deuteromethanol. The methanol served as (1) deuterium lock of magnetic field, (2) external reference, and (3) means to determine the sample temperature from the difference in the chemical shift of the signals of residual CH_3 and OH protons at the moment of recording the spectrum.

The integral intensity (area) of the ^{1}H NMR signals on cooling or heating was used for estimating the water content of the examined samples. The relatively narrow signals of residual protons in CD_3OD fall to

the region on the slope of the broad signal; therefore, the measured area included their permanent contribution. The area was normalized to the value $S = 1000 \pm 5\%$ of the integral intensity at room temperature.

The spin–lattice relaxation time was measured using the common Carr–Purcell method [20].

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