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Accepted 15 October 2003

Abstract

Carbon/silica samples prepared using mesoporous silica gel (SG, SBA-15) as a support, were subjected to the pyrolysis and hydrothermal treatment using H₂O₂ as a modifier. The adsorption of water was studied by gravimetry, quasi-isothermal titration calorimetry and ¹H NMR method. On the base of this method the energy of adsorption of strongly (C_w^s) and weak (C_w^w) adsorbed water, maximum decrease of Gibbs free energy of strongly and weakly adsorbed water (ΔG^s and ΔG^w) as well as surface free energy of the adsorbent in the aqueous medium was determined. No direct correlation was found between characteristics of the water layers adsorbed on the carbosils surface and the carbon phase content. Hydrothermal treatment affects the interactions of adsorbent surface with the aqueous phase significantly.

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Keywords: Hydrothermal treatment; Water layers; Carbosils suspensions

1. Introduction

In the last decade, the hydrothermal treatment (HTT) is widely used for the synthesis of mesoporous silica adsorbents [1–5]. The modification of their surface [6–12], by hydrothermal treatment is usually used to increase the surface area and decrease of the surface energy of the adsorbent.

allowing to determine the extent of hydrothermal treatment effect on structural parameters (sizes and volumes of pores as well as the specific surface area) [11]. The presence of carbon or metal oxides on the silica surface diminishes the effect of HTT on the surface structure [13,14]. However, in the case of complex materials, the HTT method still remains an effect tool of adsorbent structure modification.

Carbosils (CS) synthesized on the basis of mesoporous SGs [15,16] are perspective complex mesoporous adsorbents, which can be applied for adsorption of both polar and nonpolar molecules. They can be obtained by means of pyrolysis of various organic compounds on the silica surface in the flow reactor without the access of oxygen. As in the case of initial SGs, the HTT method enables modification of carbosil properties. As a result, the change of both porous structure and complex material surface group structure takes place.

The structure of water layers adsorbed on the surface is very important in application of mesoporous materials as adsorbents in the aqueous media. Due to hydrophilicity of silica and carbosils surface, the layer thickness can be from several to several scores of water molecule radii [17]. In such a case, competition between molecules of adsorbent and water exerts a significant effect on adsorption of substances from aqueous solutions. Due to the HTT, significant changes in the structure of initial centres of water adsorption can take place, which results from the partial hydrolysis of Si–O–Si bonds. As a result, changes in the structure of adsorbed water layers can also occur. Therefore, to study the effect of HTT on adsorption capacity of carbon–mineral adsorbents, it is necessary to determine the way in which HTT affects the structure of bound water.

The aim of the paper is to determine the characteristics of water layers bound in aqueous suspensions of carbosils of various carbon contents on the surface and the initial silica subjected to HTT. The investigations were carried out using ^1H NMR and thermogravimetric methods. As shown elsewhere [17] these methods allow determination of not only thickness of water layers adsorbed on the surface in a wide temperature range, but also quantities of surface free energy in

the aqueous media as well as radial functions of adhesion force changes. This paper is a continuation of earlier investigations of structure of bound water layers in powders and aqueous suspensions of carbosils [18].

2. Experimental

2.1. Materials

SG Si-60 (Schuchardt Munchen, Germany) was used as the initial material (grain fraction of 0.15–0.25 mm). Carbon-coated SG (carbosils CS) were prepared as follows: 10 g of SG was placed in a quartz rotational reactor situated in an electric furnace. A portion of SG on the bottom of the reactor was conditioned at 550 °C in a stream of deoxidized nitrogen for 1 h. Then the sample was subjected to the action of CH_2Cl_2 fed into the reactor (through a heated glass evaporator (100 °C)) using a Masterflex (Cole Palmer) pump and pyrolyzed at 550 °C. The rate of CH_2Cl_2 feeding was $0.6 \text{ cm}^3 \text{ min}^{-1}$ for 0.5, 1, 2, 3, 4 and 6 h, corresponding to different synthesized carbosils. Hydrothermal treatment of adsorbents was carried out in the stainless steel autoclave. The sample (2 g) of SG was placed in a quartz vessel in the autoclave containing 20 ml of 10% H_2O_2 solution, which was heated at 200 °C for 6 h. After modification, the samples were dried at 200 °C for 6 h (CS1-6, Table 1).

The specific surface area S_{BET} calculated according to the standard BET method [19,20], pore volume V_p (estimated at $p/p_0 \approx 0.98$, where p and

Table 1
Structural parameters of carbosils after hydrothermal treatment (HTT) at 200 °C

Adsorbent	C (wt.%)	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	V_p ($\text{cm}^3 \text{ g}^{-1}$)	R_p (Å)
SG	0	60.1	0.31	208.3
CS1	0.8	335.2	0.8	75.4
CS2	4.35	321.8	0.74	71.3
CS3	14.9	327.8	0.7	69.1
CS4	20.3	287.9	0.57	63.5
CS5	26.7	343.3	0.66	63.2
CS6	35	194.6	0.32	61.4

p_0 denote the equilibrium and saturation pressures of nitrogen, respectively) and mean radii of pores R_p and other pore parameters listed in Table 1 were determined from the nitrogen adsorption–desorption data at 77 K obtained using a Micromeritics Model ASAP 2010 (V-2.00) adsorption analyzer.

2.2. NMR investigation

For recording ^1H NMR spectra of water bound to the silica surfaces in the gas and liquid media, a high-resolution WP-100 SY (Bruker) NMR spectrometer with a bandwidth of 50 kHz was used. Relative mean errors were $\pm 10\%$ for signal intensity and ± 1 K for temperature. The technique of freezing out of water was applied to separate the bulk and interfacial water in an aqueous suspension or to distinguish water from different layers upon its adsorption onto oxides from the gas phase [17,18]. The amounts of interfacial unfrozen water (C_{ufw}) in the aqueous suspensions of adsorbents, were estimated by comparison of an integral intensity (I_{ufw}) of ^1H NMR signal of unfrozen water with that (I_c) of water adsorbed on adsorbent powder from the gas phase using a calibrated function $I_c = f(C^c)$, assuming:

$$C_{\text{ufw}} = \frac{C^c I_{\text{ufw}}}{f(C^c)}$$

or by comparing the water signals in the liquid and gas phases at 285 K. The function $f(C^c)$ was obtained on the basis of the measurements of the integral intensity for given amounts of water (C^c) adsorbed on the oxide powder surfaces from the gas phase. The signals of surface hydroxyls and water molecules from ice were not detected due to features of the measurement technique and the short time ($\sim 10^{-6}$ s) of cross-relaxation of proton in solids. The free surface energy (γ_s in mJ m^{-2}) was calculated (with relative mean error $\pm 15\%$) using the known dependence of changes in the Gibbs free energy of ice on temperature:

$$\Delta G = 0.036(273 - T) \quad (1)$$

One can assume that water is frozen ($T < 273$ K)

at the interfaces when $G = G_i$ and the value of $\Delta G = G_0 - G$ equals $\Delta G_i = G_i |_{T=273 \text{ K}} - G_i(T)$ and corresponds to a decrease in the Gibbs free energy of the interfacial water due to its interaction with the solid surfaces or polymer molecules (G_0 denotes the Gibbs free energy of the bulk undisturbed water and $\Delta G > 0$; when the Gibbs free energy of the interfacial water is lower than that of the bulk water). On the basis of this approach, one can calculate the concentrations of strongly (C_{ufw}^s) and weakly (C_{ufw}^w) bound unfrozen water, a maximal reduction of the Gibbs free energy of strongly and weakly bound water (ΔG^s and ΔG^w), and free surface energy of adsorbent in aqueous medium (γ_s):

$$\gamma_s = K \int_0^{C_{\text{ufw}}^{\text{max}}} \Delta G dC_{\text{ufw}} \quad (2)$$

where $C_{\text{ufw}}^{\text{max}}$ is the total amount of unfrozen water at $T \rightarrow 273$ K. The ΔG value in Eq. (2) is the differential Gibbs free energy, which equals the differential work of adhesion:

$$\Delta G = -W_a \quad (3)$$

Therefore, γ_s equals the total work of adhesion related to the interface between the adsorbent and liquid phases. The force value of adhesion (per m^2 of the oxide surface) can be calculated using a simple equation:

$$F = \Delta G/X \quad (4)$$

where X is the distance from the surface.

For cylindrical pores in adsorbents X value was estimated by equation:

$$X = R_p [1 - (1 - C_{\text{H}_2\text{O}}/V_\Sigma)]^{1/2} \quad (5)$$

where R_p , and V_Σ are the average pores radius and pores volume, respectively.

2.3. Thermal analysis

Thermogravimetric measurements were performed using a Derivatograph-C (Paulik, Paulik and Ergey, MOM Budapest) apparatus. Water desorption was carried out under quasi-isothermal conditions. To adsorb water vapors onto the carbosil surface at 22 °C, a weighed portion of

the adsorbent was put into desiccator containing bidistilled water for 72 h.

In the quasi-isothermal Q–TG method, samples are heated at a constant rate $\beta_0 = 2.5 \text{ K min}^{-1}$ until ‘temperature of conversion’ (if desorption rate $> 0.1 \text{ mg min}^{-1}$), and then samples are under quasi-isothermal conditions maintained with a control device. After completion of this conversion (that is after evaporation of, for example, a water portion in a defined energetic state), the temperature is increased again (but at a low value of $\beta_0 = 0.5 \text{ K min}^{-1}$, if the desorption rate $< 0.1 \text{ mg min}^{-1}$) until the temperature corresponding to the next conversion is reached.

A decrease of the free energy of adsorbed water may be determined on the basis of the temperature of its desorption under quasi-isothermal conditions. Water begins to desorb from the surface when its free energy becomes equal to that of water vapor at a given temperature (considering the changes in free energy due to the phase transition). The free energy of the water vapor is known over a wide temperature range. This energy increases practically linearly with a temperature as follows [21]:

$$\Delta G = 0.197(T - 298) \quad (6)$$

Eq. (6) can be used for determination of the size of water drop evaporated from the adsorbent pore [22]. In the simplest case it can be assumed that the SG pores possess a cylindrical shape and the water in them forms microdrops confined by two concave menisci of the radius r (the adsorbent surface is well wetted by water). For simplification the water volume in pores is assumed to be equal to the volume of the sphere of the radius equal to the pore radius r . Then there is obtained the following dependence for the water mass in pores ($m_{\text{H}_2\text{O}}$) and for the free energy of the water–air interface (Φ):

$$m_{\text{H}_2\text{O}} = \sum_i m_i = \sum_i \frac{4}{3} \pi \rho_i r_i^3 n_i \quad (7)$$

$$\Phi = \sum_i \gamma 4\pi r_i^2 n_i$$

where: r_i the radius of the drop of size r_i ; n_i , the

number of such drops; ρ and γ is the density and water surface tension, respectively.

It is known that at the concave meniscus water boiling temperature is higher with the decrease of the saturated vapor pressure. This fact was used for elaboration of the method for determination of adsorbent pore sizes from the thermogravimetric data (TGM) [23,24]. The simplest way is to use Eq. (7).

Let us assume that due to temperature change of the system, the drops of radius r_i evaporated which corresponds to the change of adsorbed water mass of size m_i and to the decrease of free energy at the water–air interface by the quantity $d\Phi$. Then:

$$d\Phi/dm_{\text{H}_2\text{O}} = 3\gamma/\rho r_i \quad (8)$$

As the Gibbs differential energy in Eq. (6) is connected with the quantity Φ by the relation:

$$\Delta G = \phi M_{\text{H}_2\text{O}}/m_{\text{H}_2\text{O}}$$

where: $M_{\text{H}_2\text{O}}$ is the water molecular mass, it is easy to determine the radius of evaporated water drop from Eq. (8). One should take into account the fact that density and water surface tension depend also on temperature:

$$\gamma = 0.21(374 - T) \text{ mJ m}^{-2}; \quad (9)$$

$$\rho = (1 - (T-0.01)/16) \times 10^6 \text{ g m}^{-3}$$

3. Results and discussion

Characteristics of the bound water layers can be determined according to the method described in [17,18]. Based on this it is possible to determine the concentration of strong (C_w^s) and weak (C_w^w) bound water, maximum decrease of Gibbs free energy of strongly and weakly bound water (ΔG^s and ΔG^w) as well as surface free energy of the adsorbent in the aqueous medium. As shown in Fig. 1 strongly bound water is this part of bound water for which significant changes of ΔG value take place in a narrow range of the C_{ufw} changes. According to this weakly bound water is this part of bound water for which in a wide range of C_{ufw} changes

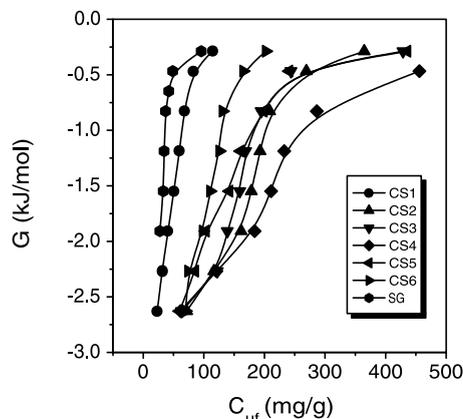


Fig. 1. Dependence of changes of unfrozen water free energy on its concentration on SG and carbosils after hydrothermal treatment (HTT).

insignificant alterations of the value ΔG are observed. The obtained results are given in Table 2.

Fig. 1 presents the dependences $\Delta G(C_{ufw})$ determined from Eq. (1) for water suspensions of hydrothermally treated SG and for the synthesized carbosils CS–HTT. With the carbon content increase, concentration of unfrozen water increases for the series of CS1–4 samples and decreases for the series of CS5–6 ones. Concentration of strongly bound water changes in an analogous way. However, it should be stressed that in the HTT process the specific surface area of coked samples decreases to a much smaller extent than the specific surface area of the initial SG (Table 1), i.e. the carbon layer protects effectively the silica surface from its hydrothermal modification. This influence of carbonization on the characteristics of bound water layers refers mainly

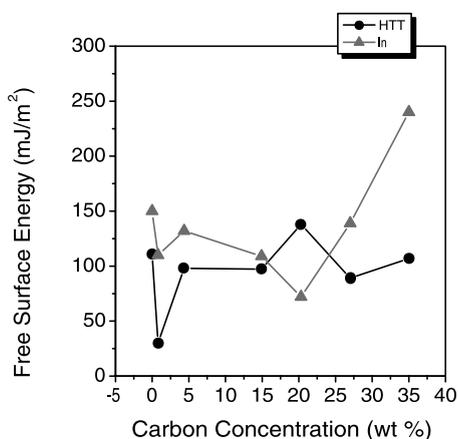


Fig. 2. Dependence of free adsorbents energy on carbon content of studies carbon silica adsorbents before and after hydrothermal treatment by means of H_2O_2 (1H NMR method).

to the surface free energy calculated from Eq. (2). The quantity γ_S reflects the total energy of adsorbent surface interaction with the aqueous medium for 1 m^2 of the surface and makes a basic parameter determining hydrophilic properties of the adsorbent in the aqueous medium [17]. The dependence $\gamma_S(C)$ is presented in Fig. 2. This figure shows analogous dependence obtained for the series of carbosils which are not hydrothermally treated and determined from the data obtained in [18].

Fig. 3 shows radial dependences of surface force values determined from Eqs. (4) and (5). On the dependences $F(X)$ there can be distinguished two components of surface forces (adhesion forces) of long and short ranges. The component of short range adhesion forces operates at the distance of 12–15 Å but that of long range at the distance of

Table 2
Parameters of bound water layers for aqueous suspensions of silica and CS (HTT) samples

Sample	ΔG^s (kJ mol $^{-1}$)	ΔG^w (kJ mol $^{-1}$)	C_w^s (mg g $^{-1}$)	C_w^w (mg g $^{-1}$)	γ_s (mJ m $^{-2}$)
SG	2.9	0.75	40	160	111
CS1	3.5	0.75	80	120	30
CS2	3.2	0.8	230	380	100
CS3	3.0	0.8	230	520	100
CS4	2.9	1.4	300	450	146
CS5	3.5	1	260	440	90
CS6	3.7	1.25	150	110	107

30–40 Å. The samples CS1 and CS4 do not confirm the general scheme. For the former the surface force values are smaller but for the latter are larger compared with other samples.

Fig. 4 presents the values $(-d(\Delta G)/dC_{ufw})$ in the function of X for the studied series of samples. The maxima on the curves of the dependences $(-d(\Delta G)/dC_{ufw})=f(X)$ correspond to these distance from the surface on which the most stable surface complexes are formed. As follows from Fig. 4 for most samples the maxima on the curves of the dependences $(-d(\Delta G)/dC_{ufw})=f(X)$ are poorly formed. The exceptions are the initial SG and the sample CS6. In the case of SG one maximum is observed but in the case of CS6-two. For these samples the most stable layers of adsorbed water

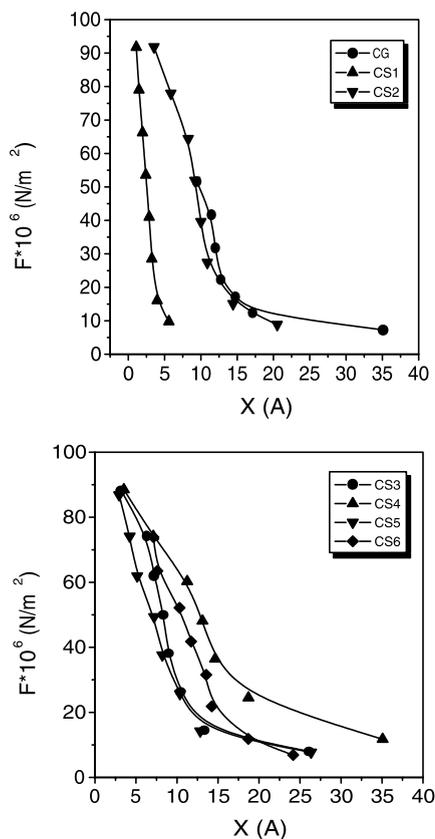


Fig. 3. Dependence of adhesion forces quantity on the distance from the surface in aqueous suspensions of carbosils (HTT) and initial SG (^1H NMR method).

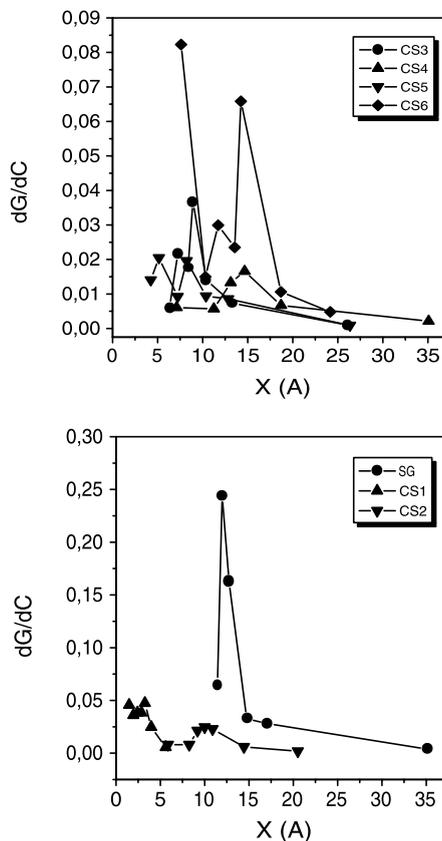


Fig. 4. Dependence of pseudochemical potential of unfrozen water on the distance from the adsorbent surface (^1H NMR method).

are 12 Å (SG) as well as 7.5 and 15 Å (CS6) thick, respectively.

As follows from Fig. 2 when the carbon concentration on the surface does not exceed 15% w/w, the character of dependence $\gamma_S(C)$ is almost identical for initial and HTT series of adsorbents, whereby for the sample CS-1 containing 0.8% of carbon on its surface there is observed a significant drop of the surface free energy which disappears at higher concentrations. At the carbon concentrations $C > 15\%$ an inverse tendency of changes of γ_S value is observed for both series of adsorbents.

A great part of surface carbon component is composed of condensed aromatic systems which react with water molecules based on the dispersion mechanism, one could expect that with the in-

crease of carbon deposit content, its hydrophilic properties decrease. The decrease of the quantity γ_S with the increase of carbon content was found earlier for another series of the adsorbents CS [25]. As follows from the data presented in Fig. 2, for all studied samples except CS-4 hydrothermal treatment in the medium of H_2O_2 leads to a decrease of total energy of adsorbent surface interaction with the aqueous medium which is clearly seen particularly at very low and very high carbon surface concentrations. These changes of hydrophilic properties of the studied samples can be explained by the fact that a large number of groups containing oxygen being the primary centers of water adsorption is formed on the carbon part of carboxylic surface during the synthesis. The existence of such centers on the carbon surface was reported many times in literature [26–29]. In such cases on the surface carbon component bound water layers of the thickness comparable with the thickness of water on the initial silica surface can be formed. That excludes dependence of hydrophilic properties on the quantity of C . As concentration of oxidized carbon groups is significant, it can change only slightly during the HTT process.

Fig. 5 presents the dependences of changes of adsorbed water free energy on its concentration for 1 m^2 surface of the adsorbent (C_w) determined from the TG data according to Eq. (6). As follows from this figure at small surface concentrations of water the curves of dependence $\Delta G(C_w)$ overlap practically. The maximum quantity of ΔG calculated in relation to free energy of water vapor at room temperature was 45 kJ mol^{-1} and in relation to free energy of water vapor at the boiling point of water was 27 kJ mol^{-1} . This quantity characterizes free energy of water adsorption under the conditions of small surface filling. It is close to the enthalpy size of formation of $O-H\cdots O$ type hydrogen bonds [30]. Such hydrogen bonds are formed on silica and carboxylic surfaces during interaction of single water molecules with them.

The intersection points of the dependence $\Delta G(C_w)$ with the axis of abscissa determine the amount of water adsorption (A_0) on the adsorbents surface under ordinary conditions. As follows from Fig. 5 coking leads to rapid decrease of

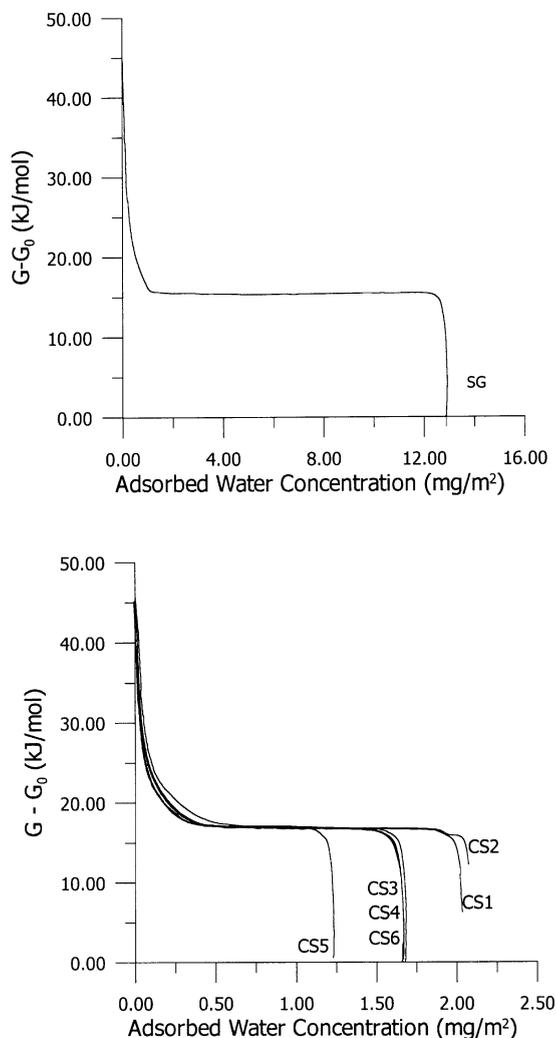


Fig. 5. Dependence of changes of free energies of water adsorbed from the air on its concentration on adsorbents surface (Q–TG method).

water vapor adsorption. For the samples CS3, CS4 and CS6 the same values A_0 are found at room temperature. For the samples CS1 and CS2 adsorption increases and for the sample CS5 decreases by about 25%. Comparing the data in Figs. 1 and 5 it can be stated that the surface of adsorbents reacts with liquid water and water vapor in a different way. This is due to the fact that in the air atmosphere the water–air interface contributes to the changes of adsorbed water free energy. This interface is determined by capillary

condensation of water in pores. Thus the differences of the value A_0 presented in Fig. 5 are determined, first of all, by the capillary condensation conditions which are the same for all studied carbosils.

Fig. 6 presents the dependences of the radius of evaporated water drop in the function of concentration of adsorbed water in the studied adsorbents calculated according to Eq. (8). Comparing these data with the sizes of average pores calculated from the adsorption measurements (Table 1), it can be concluded that in the area of large pore filling with water, the average radius of evaporated drop is close to the pore radius. Larger statistical spread of r sizes for the average section of the graph $r(C_{H_2O})$ can be caused by lack of thermo-desorption equilibrium under the conditions of quick changes of adsorbed water mass as well as by heterogeneity of hydrophilic surface centres in pores of various sizes (increase of hydrophilic surface properties is accompanied by decrease of

curvature radius of evaporated drop and vice versa).

4. Conclusions

Application of two various research methods i.e. ^1H NMR spectroscopy with low temperature treatment of liquid phase and TGM under the quasi-equilibrium conditions allows for studying interactions of water with the adsorbent surface in a wide interval of water hydration extent—from a tenth percent parts of adsorbed water to aqueous suspensions. In the aqueous medium the range of adhesion forces can change from 10 to 40 Å. However, explicit correlation between the adsorbent surface and carbon content on it was not found. When carbon concentration in carbosils is in the range $5 < C < 27\%$ w/w, hydrothermal treatment affect insignificantly the surface free energy, adhesion forces and thickness of bound

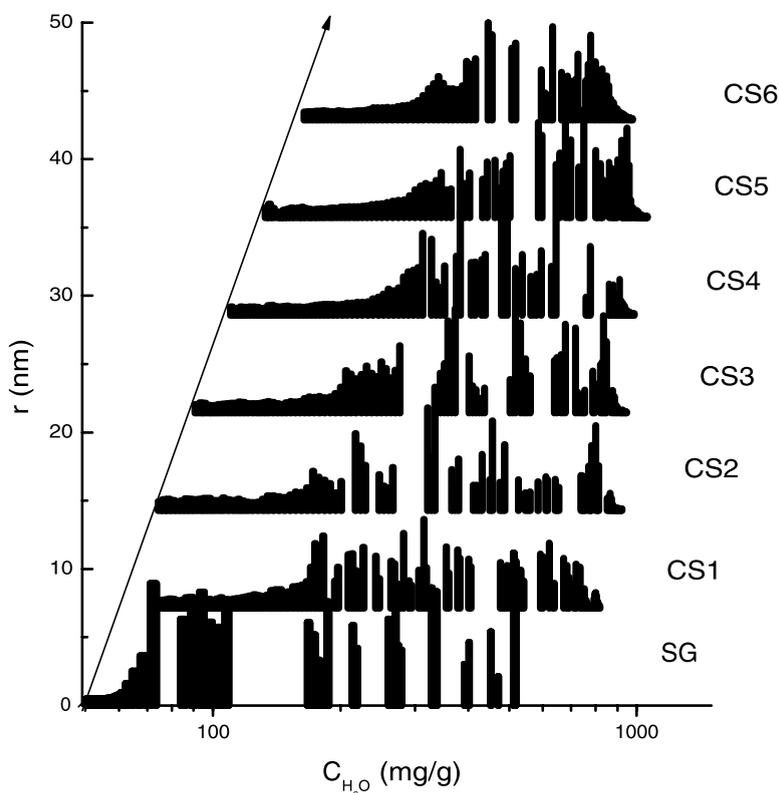


Fig. 6. Dependence of average radius of evaporated drop on the water concentration in carbosils pores and initial silica.

water layers on the carbosils surface. No changes should be expected for this type of adsorbents under the competitive conditions of sorption of dissolved substances and water on the carbosils surface compared with the initial silica. For samples of low carbon deposit concentration ($C = 0.8\%$) interactions with water became weak. Adsorbing capacity of polar substances from aqueous solutions should increase in this type of carbosils.

When the adsorbents are in contact with water vapor, their interaction with water is determined mainly by conditions of capillary condensation of water in pores. Surface carbonization leads to decrease of adsorbed water monolayers by one order of size.

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