STRUCTURAL AND ADSORPTION FEATURES OF AMORPHOUS NANOSILICA MODIFIED BY VARIOUS ADDITION OF POLYMETHYLSILOXANE

Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine
17 General Naumov Str., Kyiv, 03164, Ukraine, E-mail: v_turov@ukr.net

The aim of this study was to elucidate the effects of polymethylsiloxane (PMS) and pretreatment conditions on the behavior of bound water, as well the properties of the PMS/nanosilica blends. Amorphous nanosilica A-300 with addition of PMS hydrogel (PMS/A-300 weight ratio of 1:9 for dry matters) was studied in various dispersion media (air, chloroform alone and with addition of trifluoroacetic acid, TFAA) in comparison to PMS and A-300 alone and PMS/A-300 (1:1) using low-temperature $^1$H NMR spectroscopy and cryoporometry. Dried nanosilica and PMS alone and in the blends were characterized using microscopy, nitrogen adsorption, infrared spectroscopy, thermogravimetry, and quantum chemistry. It was shown that the properties of the blends depend not only on the components content but also on mechanical treatment causing stronger compaction of the secondary structures of nanoparticles (aggregates of nanoparticles and agglomerates of aggregates) with increasing mechanical loading. Note that a similar behavior of various blends with hydrophobic and hydrophilic nanostructured materials was observed after hydro-compaction under different mechanical loadings. Theoretical modelling shows that the structure of bound water located at a surface of hydrophilic and hydrophobic nanoparticles changes with compaction of aggregates because of changes in the confined space effects and polarity of bound water molecules. These results reflect a general regularity appearing at appropriate amount of added water and certain mechanical loading onto the blends of hydrophilic and hydrophobic nanostructured materials, which become hydrophilic but renew the hydrophobic properties after subsequent drying.

Keywords: nanosilica, polymethylsiloxane hydrogel, polymethylsiloxane/nanosilica blend, textural and morphological characteristics, mechanical loading effect, interfacial water behavior

INTRODUCTION

Unmodified and modified amorphous nanosilicas (fumed silicas) are used in various applications in industry, medicine and agriculture [1–5]. Various surface modifications of nanosilica allow one to strongly widen application fields of the materials [3–13]. One of the silica modification ways is the surface hydrophobization by such functionalities as -Si(R')₃—mRₙm (R = (CH₂)ₙCH₃, R' = Cl or OR” (R” is a short organic group) [5–7, 10]. Another way deals with adsorption or chemical modifications (e.g., hydrophobization) of fumed silica by polymers or polymer fragments [14–24]. The properties of formed polymer shells (i.e., the properties of the final materials) depend not only on chemical structure of polymers but also on their topology (1D, 2D, 3D), cross-linking degree, character of bonding (physical or chemical) to silica surface, intermolecular and intramolecular interactions, as well interactions with water which always is in real systems. The characteristics of the nanosilica/polymer blends depend on preparation conditions (dispersion media, temperature, concentration, mechanical loading, pretreatment time, etc.). These conditions can strongly affect the characteristics of the blends depending on a combination of various conditions, e.g., certain mechanical loading at certain content of water (or water and polymer). Note that the amounts of linear polymers corresponding to a monolayer coverage of nanoparticles of fumed silica A-300 (with a major fraction of nanoparticles corresponding to 9–10 nm in diameter) are in the range of 8–15 wt. % [19–21].

Poly(d)imethylsiloxane (P(D)MS) materials are of importance from a practical point of view [14–19, 25–27]. These materials are used in various applications as components of nanocomposites or co-polymers, surface modifiers, materials for chromatography, components of medicinal preparations, etc. For example, PMS hydrogel ($C_{PMS} \approx 7–10$ wt. %) is used as a medicinal oral sorbent Enterosgel.
(Kreoma-Pharm, Ukraine) [26, 27]. Note that 3D cross-linked PMS (as a “soft solid”), which has only one CH₃ group attached to each Si atom and a certain amount of residual silanols, strongly differs (in many aspects) from linear PDMS having two CH₃ groups attached to each Si atom [26–32]. The properties of PMS depend strongly on the degree of crosslinking (occurring by condensation of residual silanols from neighboring functional groups) that allows one to prepare hydrophilic PMS as a hydrogel (Enterosgel) or a hydrophobic powder after PMS drying. Clearly, the crosslinking degree increases with increasing temperature and time of drying. Various PMS are of interest from a practical point of view due to their chemical nature, softness, and strong changes in the properties upon drying-wetting-drying [22, 26, 27, 33–42].

A blend of PMS with A-300 was studied at their dry weight ratio φ = 1:1 g/g prepared using dried powders stirred with water at h = 1 g/g (as described in detail elsewhere [22]). It is of interest to analyze the behavior of a blend at the amount of PMS close to a monolayer coverage of nanosilica A-300 by linear polymers using the PMS hydrogel (however, PMS is cross-linked one and, therefore, is not linear). Therefore, the aim of this work was to study a blend of A-300/PMS (φ = 9:1 g/g and h = 1 g/g), i.e., at Cₚₘₛ = 10 wt. % close to the monolayer coverage of A-300 by linear polymers [19–21] in comparison to initial hydrogel PMS (h = 13.3 g/g), A-300 alone, and the PMS/A-300 (1:1) blend (h = 1 g/g). To reduce the effect of PMS crosslinking upon drying (due to condensation of residual hydroxyls that transforms PMS into hydrophobic 3D state), the PMS hydrogel (Cₚₘₛ ≈ 7 wt. %, C_water ≈ 93 wt. %, PMS is in a hydrophilic state with a minimal degree of cross-linking) was stirred with nanosilica A-300 at their dry weight ratio φ = 1:9 g/g and the degree of hydration at h ≈ 1 g of water per gram of dry A-300/PMS.

**MATERIALS AND METHODS**

Initial fumed amorphous nanosilica A-300 (Pilot plant of Chuiko Institute of Surface Chemistry, Kalush, Ukraine) was hydro-compacted (cA-300) using 3 g of water per 1 g of dry A-300, stirred and then dried at room temperature for several days. The bulk density of cA-300 is ρₜ ≈ 0.25 g/cm³ instead of 0.05 g/cm³ for the initial nanosilica.

Commercial polymethylsiloxane (PMS) hydrogel, synthesized using methytrichlorosilane as a precursor, at ~ 7 wt. % of PMS and 93 wt. % of water (Enterosgel, Kreoma-Pharm, Ukraine) was used as the initial material. In the hydrogel, PMS is hydrophilic because of a relatively small degree of crosslinking caused by condensation of residual silanols. After drying of PMS at room temperature for a week, the amount of water bound in PMS was small (0.7 wt. %) and it became hydrophobic (see [22]). After stirring of dried PMS with water (1:1 g/g) it becomes hydrophilic again and can form uniform suspension [22].

Initial PMS hydrogel and dried hydro-compacted nanosilica A-300 were mixed in a porcelain mortar. The content of PMS in the blend was Cₚₘₛ = 10 wt. % with respect to dry solids. The hydration degree (h) of this blend was 1 g water per gram of dry solids (h ≈ 1 g/g). If the blend was stirred without any strong mechanical loading (simple mixing) that bulk density ρₜ ≈ 0.66 g/cm³ (labelled as PMS/A-300 at the weight ratio φ = 1.9 g/g for dry matters). If the blend was stirred under strong mechanical loading (careful grinding in a porcelain mortar with strong hand-loading giving ~ 20 atm, estimated from the geometry of the mortar and a pestle used and a loading weight, for 15 min) that ρₜ ≈ 0.80 g/cm³. This is a hydro-compacted blend labeled as cPMS/A-300 (φ = 1.9 g/g). The blends PMS/A-300 and cPMS/A-300 were compared to initial hydrogel PMS (7 wt. %), as well the PMS/A-300 and cPMS/A-300 blends (φ = 1:1 g/g) (prepared using dried components stirred with water at h = 1 g/g) located in different dispersion media (air, CDCl₃, and CDCl₃ with addition of deuterated trifluoroacetic acid CF₃COOD, TFAA). Hydro-compaction of a set of nanomaterials based on unmodified and modified (hydrophobized) nanooxides was described in detail elsewhere [22, 43–46].

A TEM study was performed using a TECNAI G2 F30 microscope (FEI–Philips, Holland) at the operating voltage of 300 kV. The powder samples were added to acetone (chromatographic grade) and sonicated. A drop of the suspension was then deposited on a copper grid with a thin carbon film. After acetone
evaporation, sample particles remained on the film were studied with TEM.

A SEM study of dried powder samples was performed using a FE-SEM (Hitachi S-4700, Japan) at the operating voltage of 15 kV at the magnification range of 5000–100000.

To analyze the textural characteristics of dried PMS, PMS/A-300(1), and A-300 degassed at 453 K for 12 h, low-temperature (77.4 K) nitrogen adsorption-desorption isotherms were recorded using a Micromeritics ASAP 2010 adsorption analyzer. The specific surface area (Table 1, S_{BET}) was calculated according to the standard BET method [47]. The total pore volume (Table 1, V_p) was evaluated from the nitrogen adsorption at p/p_0 ≈ 0.98–0.99, where p and p_0 denote the equilibrium and saturation pressure of nitrogen at 77.4 K, respectively [48]. The differential (f(R) = dV/dr) pore size distributions (PSD) were calculated using a nonlocal density functional theory (NLDFT, Quantachrome software) method with a model of cylindrical pores in silica [49]. Incremental PSD (IPSD, V(R) = f(R) + f(R+1)/2 at ΣV(R) = V_p) were calculated using a complex model of pores (such as slit-shaped and cylindrical pores and voids between nanoparticles of silica or polymer, a SCV model) with a self-consistent regularization (SCR) procedure [50].

Low-temperature ¹H nuclear magnetic resonance (NMR) spectra of static samples (placed into 4 mm and 5 mm NMR ampoules) of initial PMS hydrogel (h = 13.3 g/g), dry powders hydrated at h = 1.0 g water per gram of dry PMS, A-300, or PMS/A-300 (ρ = 1:9 and 1:1 g/g) (preheated at 433 K) were recorded using a Varian 400 Mercury spectrometer (magnetic field 9.4 T, bandwidth 20 kHz) utilizing eight 90° probe pulses of 3 μs duration. Relative mean errors were less than ±10% for ¹H NMR signal intensity for overlapped signals, and ±5% for single signals; therefore, the average errors in estimations of the amounts of unfrozen water vs. temperature are about ±5%. Temperature control was accurate and precise to within ±1 K. The accuracy of integral intensities was improved by compensating for phase distortion and zero-line nonlinearity with the same intensity scale at different temperatures. To prevent supercooling of water in the samples, the beginning of spectra recording was at 200 K. The samples precooled to this temperature for 10 min were then heated to 280 K at the rate of 5 K/min with steps ΔT = 10 K or 5 K at the heating rate of 5 K/min for 2 min. They were maintained at a fixed temperature for 5 min, and for data acquisition at each temperature, for 1 min. The applications of the low-temperature ¹H NMR spectroscopy and NMR cryoporometry, based on the freezing point depression of liquids located in pores depending on the pore sizes, to numerous objects were described in detail elsewhere [19, 51–53]. Note that solids (PMS, silica, ice) do not contribute the ¹H NMR spectra recorded here due to a large difference in the transverse relaxation times of liquid water and immobile solid components and due to a narrow bandwidth (20 kHz) of the spectrometer used [19].

The infrared (IR) spectra of PMS and PMS/A-300(1) were recorded for air-dry samples in the ranges of 4000–1200 cm⁻¹ (pellets of 20 mg pressed at 2000 atm) using a Specord M80 (Carl Zeiss). To record the IR spectra, samples with PMS were dried at room temperature for 48 h. The transmittance spectra were recorded with 4 cm⁻¹ steps and integration time of 3 s.

The δ_h values for water clusters (up to 100H₂O) were calculated as the difference in the isotropic values of the magnetic shielding tensors of H atoms (σ_{H,iso}) of tetramethylsilane, TMS (δ_{H,TMS} = 0 ppm) as a reference compound (e.g. σ_{H,iso} = 31.76 and 31.40 ppm for tetramethylsilane (TMS) by GIAO/B3LYP/6-31G(d,p) and GIAO/6B97X–D/cc-pVDZ [54], respectively) and a given compound using equation [54]

\[
\delta_h = \frac{1}{3} Tr \sigma_{H,TMS} - \frac{1}{3} Tr \sigma_h,
\]

where Tr is the trace of matrix, since σ is the tensor with nine elements. The distribution functions of the δ_h values were calculated using a simple equation

\[
f(\delta_h) = (2\pi\sigma^2)^{-0.5}\sum_j \exp\left[-(\delta_h - \delta_{j}\sigma)^2 / 2\sigma^2\right],
\]

where j is a number of H atom, σ is the distribution dispersion, and δ_j is the calculated value of the j-th H atom. Large structures (Fig. 9) were calculated using the PM7 method (MOPAC 2016 package with GPU/CUDA) [55, 56]. To calculate the f(δ_h) functions using
the PM7 results, a calibration function was used to describe the dependence between atomic charges \( q_H \) (PM7) and the \( \delta_H \) values (GIAO/\( \omega \)B97X-D/cc-pVDZ) for water clusters \( \delta_H = -27.38435372 + 83.67491184 \times q_H \). This function was used to calculate the \(^1\)H NMR spectra of water clusters bound to PMS. Visualization of the calculated structures was carried out using ChemCraft [57] or Avogadro 2 (v. 1.91) [58] program suits.

RESULTS AND DISCUSSION

Mechanical loading affects the distribution of PMS and A-300 nanoparticles in their wetted-dried blends (Figs. 1 and 2), as well the organization of secondary particles and the textural characteristics of the wetted-dried blends or A-300 and PMS alone (Table 1).

Note that PMS nanoparticles (2–4 nm in radius) are smaller than A-300 ones (4–6 nm in radius) [22]. Therefore, the specific surface area of the latter is lower (Table 1, \( S_{BET} \)). Additionally, secondary particles of PMS and A-300 are differently organized (Fig. 1 a, b) due to the formation of chemical bonds between nanoparticles of PMS (upon sol-gel synthesis at room temperature [17, 26, 27]) and mainly physical bonding of silica nanoparticles (flame synthesis at \( T > 1200 \, \text{K} \) [3–5]). cPMS/A-300\(_{11}\) stirred under high mechanical loading demonstrates more compacted secondary structures (Fig. 1 d) than that of the blend prepared without strong mechanical loading PMS/A-300\(_{11}\) (Fig. 1 c). The changes in the organization of secondary particles can strongly influence the confined space effects important for such adsorbates as water, which can be unfrozen in pores at \( T < 273 \, \text{K} \) [19]. The samples stirred with added water and dried (and degassed before the nitrogen adsorption measurements) demonstrate mainly a mesoporous character (Table 1, \( V_{meso}, S_{meso} \) calculated at \( 1 \, \text{nm} < R < 25 \, \text{nm} \) in pore radius) with a small contribution of nanopores \( (V_{nano}, S_{nano} \) at \( 0.35 \, \text{nm} < R < 1 \, \text{nm} \)).

The infrared (IR) spectra (Fig. 3) as well the thermogravimetry data [22] confirm that the amounts of water in air-dried PMS (located in air) are small because it is hydrophobic. Note that water is removed from the initial hydrogel upon heating (TG measurements) up to 200 °C at a maximal evaporation rate at 107 °C [22]. This suggests that a major fraction of water in the hydrogel is bound but with main contribution of weakly bound water (WBW) (\textit{vide infra}).

Fig. 1. TEM images of (a) PMS, (b) A-300, (c) PMS/A-300\(_{11}\), and (d) cPMS/A-300\(_{11}\) (scale bar 50 nm)
Table 1. Textural characteristics of dried-degassed PMS alone and PMS/A-300

| Sample                  | $S_{BET}$, m$^2$/g | $S_{DFT}$, m$^2$/g | $S_{Nano}$, m$^2$/g | $V_p$, cm$^3$/g | $V_{Nano}$, cm$^3$/g | $V_{Meso}$, cm$^3$/g | $V_{Macro}$, cm$^3$/g | $\langle R_V \rangle$, nm | $\langle R_S \rangle$, nm |
|-------------------------|---------------------|--------------------|---------------------|-----------------|---------------------|---------------------|---------------------|----------------------|----------------------|
| PMS                     | 507                 | 471                | 2                   | 504             | 1.320               | 0.002               | 1.304               | 0.014                | 6.08                 | 5.28                 |
| Stirred PMS             | 572                 | 581                | 1                   | 558             | 2.604               | 0.001               | 2.248               | 0.355                | 16.86                | 9.42                 |
| PMS/A-300               | 354                 | 322                | 35                  | 306             | 1.265               | 0.019               | 1.084               | 0.163                | 15.25                | 7.64                 |
| cPMS/A-300              | 407                 | 357                | 8                   | 399             | 1.021               | 0.006               | 1.005               | 0.011                | 6.56                 | 5.17                 |
| A-300                   | 294                 | 289                | 44                  | 229             | 0.850               | 0.023               | 0.567               | 0.259                | 20.41                | 6.14                 |

Note. The values of $V_{Nano}$ and $S_{Nano}$, $V_{Meso}$ and $S_{Meso}$, and $V_{Macro}$ and $S_{Macro}$ were calculated by integration of the $f_V(R)$ and $f_S(R)$ functions at $0.35 \, nm < R < 1 \, nm$, $1 \, nm < R < 25 \, nm$, and $25 \, nm < R < 100 \, nm$, respectively. The values of $\langle R_V \rangle$ and $\langle R_S \rangle$ as the average pore radii were calculated as a ratio of the first moment of $f_V(R)$ or $f_S(R)$ to the zero moment (integration over the 0.35–100 nm range) $\langle R \rangle = \int f(R)RdR/\int f(R)dR$

Fig. 2. SEM images of degassed (a) Enterosgel, (b) PMS dried at room temperature, (c) PMS/A-300, and (d) cPMS/A-300 (scale bar 1 \( \mu \)m)

Low-temperature (200 K < $T$ < 273 K) $^1$H NMR spectroscopy of static samples gives additional information on the temperature and interfacial behaviors of water bound in the PMS hydrogel, dried-wetted PMS, initial and compacted A-300, and pretreated PMS/A-300 blends depending on a pretreatment type and dispersion media (Figs. 4–6, Tables 2 and 3). Note that the $^1$H NMR signal shapes demonstrate certain distortion and asymmetry, especially at low temperatures, due to the presence of various bound water structures (clusters and domains located in voids (pores) of various shapes and sizes), as well nonuniform signal broadening due to nonuniform filling of NMR ampoules by a sample [19, 59].

Fig. 3. Infrared spectra of air-dried cPMS/A-300, PMS, and PDMS alone in the range of 4000–1300 cm$^{-1}$
The $^1$H NMR spectra of the PMS hydrogel in the chloroform dispersion medium strongly differ from those for the air/water dispersion media (Fig. 4a) since the signals become narrow and intensity faster decreases with decreasing temperature. This suggests that chloroform can displace water from voids in PMS aggregates to form larger domains, which can be frozen at higher temperatures. In other words, contributions of WBW and unbound water (UBW) become larger in the chloroform dispersion medium. This is well visible in the changes in the dependence of the amount of unfrozen water ($C_{uw}$) vs temperature (Fig. 5a). Note that changes in pretreatment of PMS (drying, wetting, stirring) and dispersion media composition affect the $^1$H NMR spectra [22] and changes in contents of WBW (frozen at $260 \text{ K} < T < 273 \text{ K}$) and strongly bound water, SBW (frozen at $T < 260 \text{ K}$), as well strongly (SAW at $\delta_1 = 4–6 \text{ ppm}$) and weakly (WAW at $\delta_1 = 1–2 \text{ ppm}$) associated waters [19]. Note that only SAW is observed for the PMS hydrogel and hydrated PMS/A-30019 (Fig. 4).

The interfacial and temperature behaviors of water bound in PMS/A-30019 (Fig. 4b–d) or PMS/A-30011 [22] at $h = 1 \text{ g/g}$ become more complex in comparison to those for PMS alone (Fig. 5a).

This is caused by the difference in the interactions of water with PMS and nanosilica (due to the difference in their surface structure), as well by the organization of water clusters and domains in various voids between different nanoparticles (Fig. 7). For example, in the chloroform medium, besides main signal at $\delta_1 = 4.5–5.5 \text{ ppm}$ (Fig. 8a, s1), there is an additional signal at 7.3–7.7 ppm appearing at low temperature (Fig. 8a, s2). The latter corresponds to SBW/SAW.

![Fig. 4. $^1$H NMR spectra recorded at different temperatures for (a) initial PMS hydrogel in air (1, solid lines) and CDCl$_3$ (2, dotted-dashed lines); (b, d) PMS/A-30019 at $h = 1 \text{ g/g}$ in air (1, solid lines) and CDCl$_3$ (2, dotted-dashed lines) (d) shows the spectra at low temperatures; (c) cPMS/A-30019 at $h = 1 \text{ g/g}$ in air (1, solid lines), CDCl$_3$ (2, dotted-dashed lines), and CDCl$_3$/TFAA (7:1) (3, solid lines)]
Structural and adsorption features of amorphous nanosilica modified by various addition of polymethylsiloxane

Fig. 5. The amounts of unfrozen water ($C_{uw}$) vs temperature for (a) initial PMS hydrogel in air and CDCl$_3$; (b) cPMS/A-300, and PMS/A-300 at $h = 1$ g/g in air, CDCl$_3$, and CDCl$_3$/TFAA (7:1).

Fig. 6. Relationships between the amounts of unfrozen water ($C_{uw}$) and changes in the Gibbs free energy ($\Delta G$) of this water depending on temperature for (a) initial PMS hydrogel being in air or chloroform medium, and (b) PMS/A-300 (1:9) blend hydrated at $h = 1$ g/g with high mechanical loading (cPMS/A-300 at bulk density $\rho_b = 0.8$ g/cm$^3$) and low mechanical loading (PMS/A-300 at $\rho_b = 0.66$ g/cm$^3$) being in air, chloroform or CDCl$_3$/TFAA (7:1) dispersion media.

Addition of TFAA affects the $\delta_H$ values and freezing temperature due to the colligative properties [60] of the acid solution (Fig. 2 c, lines 3). However, the $\delta_H$ values are smaller than that observed for pure TFAA solution at $\delta_H \approx 11$ ppm characteristic for strong acids [59]. This effect could be explained by reduced activity of bound water as a solvent [19]. In other words, bound water can poorly dissolve even TFAA. The amount of SBW in the initial PMS (7 wt. %) hydrogel is $C_{uw}^{s} = 0.7$ g per gram of dry PMS (Table 2). In the chloroform medium, the $C_{uw}^{s}$ value strongly decreases because chloroform can displace water from voids between PMS nanoparticles to reduce the contact area between immiscible liquids [19]. In the hydrogel, the total content of water $h \approx 13.3$ g/g is greater than the amounts of SBW+WBJ (Table 1, $C_{uw}^{s}+C_{uw}^{w}$) both for chloroform or air dispersion media because a fraction of water is unbound water (UBW), which is frozen at $T \approx 273$ K. Addition of chloroform affecting the bound water organization leads to a decrease in the values of $\gamma_S$ (as a modulus of total changes in the Gibbs free energy of bound water), amounts of SBW ($C_{uw}^{s}$) and WBW($C_{uw}^{w}$), specific surface area in contact with bound unfrozen water in mesopores ($S_{meso,uw}$), average radius of unfrozen water clusters located in mesopores $<R_{meso,uw}>$, and to an increase in the average melting
Similar effects in the re-organization of bound unfrozen water in the chloroform dispersion medium are observed for PMS/A-300 (Tables 2 and 3). However, a much lower value of $h = 1 \text{ g/g}$ (instead of 13.3 g/g) results in disappearing of UBW. Therefore, addition of chloroform reduces the $C_{uw}^s$ value and enhances contribution of WBW (Tables 2 and 3, $C_{uw}^w$). However, these changes depend on the pretreatment type of the blends.

For strongly treated cPMS/A-300$_{19}$ ($h = 1 \text{ g/g}$) located in air, the $C_{uw}^s$ value is greater than that for PMS/A-300$_{19}$ (Table 2) that corresponds to greater values of $\gamma_S$, $S_{nano,uw}$, $S_{meso,uw}$ and lower values of $<T_m>$, $<R_{nano,uw}>$, $<R_{meso,uw}>$, despite the $V_{meso,uw}$ value is smaller. However, in the chloroform medium, the values of $C_{uw}^s$ and $\gamma_S$ decrease stronger for cPMS/A-300$_{19}$, but a diminution of the $V_{meso,uw}$ value is smaller than that for PMS/A-300$_{19}$. The character of these changes is well observed in changes in the PSD (Fig. 7 (c)) and IPSD (Fig. 7 (d)) corresponding to the size distribution of unfrozen water located in various pores (voids between nanoparticles). In contrast to the PMS hydrogel (Fig. 7 a, b), changes in the PSD and IPSD are more complex for composite systems. The re-organization of nanoparticles in secondary structures during strong mechanical loading (Figs. 1 and 2) affects the interfacial and temperature behaviors of bound water due to changes in the size distributions of voids; i.e., the confined space effects change.

Changes in the $<T_m>$ and $\gamma_S$ values (Tables 2 and 3, Fig. 9) give clear pictures on the strength of interactions of unfrozen water with surroundings depending on several factors such as adsorbent composition, water content, pretreatment type, and dispersion medium. However, there is no linear or monotonic correlations between the $<T_m>$ and $\gamma_S$ values because the former is determined from the $C_{uw}(T)$ function, but the latter is determined from the $\Delta G(T)$ function, and the relationship between the $C_{uw}(T)$ and $\Delta G(T)$ functions is not linear (Figs. 5 and 6). The maximum $\gamma_S$ value is observed for the initial PMS hydrogel.

Fig. 7. (a, c) Differential and (b, d) incremental size distributions of pores (voids between nanoparticles) filled by unfrozen water for (a, b) initial PMS hydrogel in air and CDCl$_3$; (c, d) cPMS/A-300$_{19}$ and PMS/A-300$_{19}$ at $h = 1 \text{ g/g}$ in air, CDCl$_3$, and CDCl$_3$/TFAA (7:1)
### Table 2. The characteristics of bound water unfrozen at \( T < 273 \) K for PMS and blends with PMS/A-300 treated at low and high mechanical loading

| Sample          | Medium  | \( C_{uw}^w \), mg/g | \( C_{uw}^w \), mg/g | \( -\Delta G_s \), kJ/mol | \( \gamma_S \), J/g | \( <T_m> \), K | \( S_{nano,uw} \), m²/g | \( S_{meso,uw} \), m²/g | \( S_{macro,uw} \), m²/g | \( V_{nano,uw} \), cm³/g | \( V_{meso,uw} \), cm³/g | \( V_{macro,uw} \), cm³/g | \( <R_{nano,uw}> \), nm | \( <R_{meso,uw}> \), nm | \( <R_{macro,uw}> \), nm |
|-----------------|---------|----------------------|----------------------|--------------------------|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| PMS gel         | Air/water | 700                  | 5767                 | 2.04                      | 113.1           | 265.35         | 0              | 476            | 0              | 0              | 6.467          | 0              | 2.122          | 0              | 22.46          | 17.08          | 80.59          |
| PMS/A-300₁₀     | CDCl₃   | 100                  | 4230                 | 0.58                      | 30.2            | 268.91         | 0              | 248            | 52             | 0              | 2.122          | 0              | 0.91           | 0.91           | 19.78          |                |                |
| Low loading     | Air      | 125                  | 875                  | 2.82                      | 13.6            | 263.20         | 18             | 34             | 0              | 0.008          | 0.307          | 0.15           | 0.89           | 0.89           | 17.88          |                |                |
| PMS/A-300₁₀     | CDCl₃   | 65                   | 935                  | 3.17                      | 9.0             | 262.62         | 29             | 64             | 0              | 0.013          | 0.467          | 0.90           | 0.90           | 14.47          |                |                |
| High loading    | CDCl₃   | 60                   | 940                  | 2.86                      | 7.9             | 262.42         | 9              | 33             | 0              | 0.004          | 0.283          | 0.90           | 0.90           | 16.96          |                |                |
| PMS/A-300₁₀     | CDCl₃+  | 300                  | 700                  | 2.55                      | 26.2            | 256.08         | 32             | 93             | 0              | 0.015          | 0.732          | 0.93           | 0.93           | 15.69          |                |                |

*Note. \( C_{uw}^w \) and \( C_{uw}^w \) are the amounts of weakly and strongly bound waters; \( \Delta G_s \) is the changes in the Gibbs free energy of water layer closely located to a surface; \( \gamma_S \) is the modulus of the total changes in the Gibbs free energy of bound water unfrozen at \( T < 273.15 \) K; \( <T_m> \) is the average melting temperature; \( S_{nano,uw} \) and \( V_{nano,uw} \), \( S_{meso,uw} \) and \( V_{meso,uw} \) are the specific surface area and pore volume of nanopores at \( 0.2 \text{ nm} < R < 1 \text{ nm} \) and mesopores at \( 1 \text{ nm} < R < 25 \text{ nm} \), respectively, in contact with unfrozen water.

### Table 3. Characteristics of water (\( h = 1.0 \text{ g/g} \)) bound to non-compacted and compacted PMS alone and with A-300 (\( \varphi = 1:1 \)) in air, chloroform medium alone or with addition of TFAA, and hydro-compacted nanosilica cA-300

| Sample          | Medium  | \( C_{uw}^w \), mg/g | \( C_{uw}^w \), mg/g | \( -\Delta G_s \), kJ/mol | \( \gamma_S \), J/g | \( <T_m> \), K | \( S_{nano,uw} \), m²/g | \( S_{meso,uw} \), m²/g | \( V_{nano,uw} \), cm³/g | \( V_{meso,uw} \), cm³/g | \( \gamma_S \), J/g | \( S_{nano,uw} \), m²/g | \( S_{meso,uw} \), m²/g | \( V_{nano,uw} \), cm³/g | \( V_{meso,uw} \), cm³/g | \( S_{meso,uw} \), m²/g | \( V_{nano,uw} \), cm³/g | \( V_{meso,uw} \), cm³/g |
|-----------------|---------|----------------------|----------------------|--------------------------|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| PMS             | Air     | 280                  | 720                  | 2.48                     | 25.13           | 258.63         | 138            | 98             | 0.056          | 0.758          | 0.001          | 0.007          | 0.006          | 0.796          | 0.008          | 0.041          |                |                |
| PMS             | CDCl₃   | 10                   | 990                  | 2.44                     | 0.69            | 262.36         | 3              | 1              | 0.001          | 0.007          |                |                |                |                |                |                |                |                |
| PMS             | CDCl₃/TFAA | 475                | 525                  | 2.45                     | 27.73           | 257.39         | 15             | 226            |                |                |                |                |                |                |                |                |                |                |
| cA-300*         | Air     | 40                   | 1085                 | 2.41                     | 7.22            | 268.1          | 4              | 48             | 0.002          | 0.710          |                |                |                |                |                |                |                |                |
| cA-300*         | CDCl₃   | 30                   | 1095                 | 2.53                     | 6.10            | 268.4          | 10             | 44             | 0.005          | 0.626          |                |                |                |                |                |                |                |                |
| PMS/A-300       | Air     | 115                  | 885                  | 2.85                     | 12.06           | 257.04         | 64             | 86             | 0.026          | 0.297          |                |                |                |                |                |                |                |                |
| PMS/A-300       | CDCl₃   | 95                   | 25                   | 3.04                     | 2.88            | 251.26         | 20             | 14             | 0.008          | 0.041          |                |                |                |                |                |                |                |                |
| (SAW)           |         |                      |                      |                          |                 |                |                |                |                |                |                |                |                |                |                |                |                |                |
| PMS/A-300       | CDCl₃   | 795                  | 95                   | 2.77                     | 9.91            | 257.88         | 52             | 54             | 0.021          | 0.202          |                |                |                |                |                |                |                |                |
| (WAW)           |         |                      |                      |                          |                 |                |                |                |                |                |                |                |                |                |                |                |                |                |
| ePMS/A-300      | Air     | 225                  | 775                  | 2.68                     | 17.45           | 261.78         | 110            | 70             | 0.044          | 0.675          |                |                |                |                |                |                |                |                |
| ePMS/A-300      | CDCl₃   | 30                   | 970                  | 2.90                     | 5.01            | 263.69         | 31             | 20             | 0.012          | 0.207          |                |                |                |                |                |                |                |                |

*Note. \( C_{uw}^w \) and \( C_{uw}^w \) are the amounts of weakly and strongly bound waters; \( \Delta G_s \) is the changes in the Gibbs free energy of water layer closely located to a surface; \( \gamma_S \) is the modulus of the total changes in the Gibbs free energy of bound water unfrozen at \( T < 273.15 \) K; \( <T_m> \) is the average melting temperature; \( S_{nano,uw} \) and \( V_{nano,uw} \), \( S_{meso,uw} \) and \( V_{meso,uw} \) are the specific surface area and pore volume of nanopores at \( R < 1 \text{ nm} \) and mesopores at \( 1 \text{ nm} < R < 25 \text{ nm} \), respectively, in contact with unfrozen water. *\( h = 1.125 \text{ g/g} \)
Any treatment or addition of chloroform, a decrease in water content or addition of nanosilica results in a decrease in the $\gamma_S$ value; i.e., the integral interactions of water with surrounding decrease. One of the main factors of this general effect is a decrease in the surface area of contacts between water and polar functionalities of solids (e.g., $S_{\text{meso,uw}}$ (Table 2) is maximal for the initial PMS hydrogel). Note that PMS is hydrophilic in the initial hydrogel (due to residual silanols) in contrast to dried PMS, in which a number of residual silanols decreases due to condensation that results in the hydrophobic properties of the dried powder [22]. The second important factor is that the specific surface area of hydrated, dried, stirred-dried PMS is much greater than that of initial or hydro-compacted A-300 (Table 1). Therefore, the same amounts of A-300 nanoparticles can interact with a smaller amount of water than that for the PMS nanoparticles.

Note that dried PMS is mainly mesoporous with a very small contribution of nanopores (Table 1). Therefore, at $h = 1$ g/g, chloroform can strongly displace water from PMS that results in a minimal value of $\gamma_S$ (Fig. 9, Tables 2 and 3). However, wetting of air-dried PMS results in appearance of nanopores (Table 3, $S_{\text{nano,uw}}$). Chloroform can displace this water from nanopores; therefore, the $S_{\text{nano,uw}}$ value strongly reduces. In the case of hydro-compacted ca-300 alone, the effects of chloroform is lower, and the $S_{\text{nano,uw}}$ value even increases from 4 to 10 m$^2$/g, and $S_{\text{meso,uw}}$ decreases only slightly (from 48 to 44 m$^2$/g). For PMS/A-300$_{11}$ (Table 3) and PMS/A-300$_{19}$ (Table 2) at $h = 1$ g/g, the chloroform effects on bound water are greater than that for A-300 alone (Tables 2 and 3, Figs. 4–6, 9).

For the values of $\delta_H$, there is a general tendency in an increase in $\delta_H$ with decreasing temperature (Fig. 8 $a$, $b$). This is due to several
reasons such as decreasing mobility of the molecules tending to spatial positions corresponding to them in ice (for ice Ih $\delta_H \approx 7$ ppm but for bulk water $\delta_H \approx 4.5–5.5$ ppm), ordering water structure with decreasing contribution of interstitial water; and decreasing vibrational and rotational mobility of the bonds and functional groups. However, there are such additional factors affecting the $\delta_H (T)$ course as changes in surroundings with appearing nonpolar co-adsorbate/dispersion medium, changes in the pore (void) topology depending on adsorbent composition, formation of ice crystallites in pores that affects the pore shape. These effects lead to nonlinear $\delta_H$ dependence on temperature because the mentioned above factors depend differently on temperature. Note that for PMS/A-30019 and cPMS/A-30016, WAW ($\delta_H = 1–2$ ppm) is practically absent (Figs. 4 and 8) in contrast to the PMS/A-30011 blends [22]. This effect can be explained by a smaller content of the hydrophobic functionalities with decreasing content of PMS in the blends because water at a mosaic hydrophobic/hydrophilic surfaces can be present the WAW form [19, 61, 62].

Melting of ice crystallites (with an endothermic effect) leads to increased entropy of the system. Changes in the entropy of bound water/ice ($s(T)$) demonstrate several peaks (Figs. 8 c, d) due to the presence of several types of ice/bound water structures. The position of these peaks depends on several factors (water content, confined space effects – PSD, organization of PMS and A-300 nanoparticles in aggregates and agglomerates of aggregates, dispersion media type, presence of TFAA). Smaller $h$ and pore sizes or addition of TFAA result in the $s(T)$ peak shift toward lower temperatures, but the chloroform appearance gives the opposite effect. As a whole, these changes are in agreement with changes in the $\gamma_s$ values.

Theoretical calculations (Fig. 10) show that interactions of water clusters with hydrophobic PMS functionalities (corresponding to hydrophobic hydration [63–65]) are weaker than those with silanols or other water molecules. This result corresponds to a tendency of the formation of larger water structures (clusters, domains) upon interaction with hydrophobic surroundings. However, for the water shell around a non-dehydrated PMS particle (19 structural units with 60 OH groups), the $^1$H NMR spectrum is similar to that for the shell around the dehydrated PMS particle (with residual 9 OH groups). This effect is due to the clusterization of the water shells for both particles that can result in the appearance both of SAW and WAW structures in the adsorption layer. Interaction energy ($\Delta E_t$) in the system with dehydrated PMS particle (19 structural units with residual 9 OH groups) surrounded by a water shell clustered is $\Delta E_t = -19.1$ kJ/mol per a water molecule. The interaction between the water shell and PMS particle (per a water molecule) gives $\Delta E_t = -7.1$ kJ/mol, but in the water shell per se, it is stronger $\Delta E_t = -12.0$ kJ/mol.

Fig. 9. Changes in the $\gamma_s$ values of bound water depending on adsorbent composition, water content, pretreatment type, and dispersion medium
CONCLUSION

Drying of initial PMS hydrogel results in the formation of a hydrophobic powder. However, the powders of dried hydrophobic PMS alone or in a blend with hydrophilic nanosilica can be easily rehydrated upon stirring with water at $h = 1$ g/g. The properties of the blends depend on the components content and mechanical treatment due to stronger compaction of the PMS/A-300 secondary structures with increasing mechanical loading. Note that a similar behavior of the blends with hydrophobic and hydrophilic nanostructured materials was observed for several compositions [22, 32, 43–46] as well the effects during hydro-compaction [56] that reflect in a general regularity appearing at appropriate amounts of added water and certain mechanical loading onto the blends of hydrophilic and hydrophobic nanomaterials. This pretreatment results in the reorganization of the secondary structures and removal of micro-scaled air bubbles bound to hydrophobic components in an initial mixture wetted. Note that after drying of wetted-stirred blends, the powders can demonstrate the hydrophobic properties, which however disappear after subsequent wetting-stirring.

A fraction of water bound to initial PMS ($h = 13.3$ g/g) or dried-wetted PMS ($h = 1$ g/g) or dried-wetted PMS/A-300 ($h = 1$ g/g) located in air corresponds to strongly bound water frozen at $T < 260$ K, but practically entire water is strongly associated and characterized by the chemical shift at $\delta_{1} = 4.5–5.0$ ppm. If these systems are located in the hydrophobic chloroform dispersion medium, the organization of bound water strongly changes to reduce the contact area between immiscible liquids. Typically, chloroform can displace adsorbed water into narrow nanopores (inaccessible for larger chloroform molecules) or/and into larger pores (to reduce the contact area between them). In the systems studied, narrow pores give a minor contribution; therefore, chloroform displaces water mainly into larger pores. This results in a decrease in the amounts of SBW. A fraction of weakly associated water ($\delta_{1} = 1–2$ ppm), i.e., strongly clustered water with 1D and 2D structures, appears in PMS/A-30019 undergoing low mechanical loading. In PMS/A-30019 or after stronger mechanical loading on PMS/A-30011, only strongly associated water is observed due to (i) a small content of hydrophobic functionalities in the former, or (ii) changes in the confined
space effects in more strongly compacted secondary particles for the latter.

If trifluoroacetic acid is added to the chloroform medium, the colligative and confined space effects overlap and the amount of SBW increases. Note that in this case, the changes in the porosity caused by the appearance of the ice crystal in interparticle voids can be smaller than those in the systems with a main fraction of SAW/WBW.

The PMS/nanosilica blends at various weight ratio can be of interest from a practical point of view for applications as medical sorbents or preparation for agriculture applications [26, 27, 57]. The blends can be with improved or better controlled textural and adsorption characteristics, which can be easily varied in a broader range due to changes in composition and pretreatment conditions. Note that tests of these systems in various applications were started, and some promised results were obtained. In the future, it will be of interest to generalize the interfacial phenomena related to nanostructured blends of various hydrophilic and hydrophobic nanoparticles of various origin and nature.

ISSN 2079-1704. ХФТП 2019. Т. 10. № 3  215
Смещение разных свойств они воды нанокремнезем 9.

1. Zhu Y., Chen L., Zhang C., Guan Z. Preparation of hydrophobic antireflective SiO2 coating with deposition of nanoparticles on polymer surface. Appl. Surf. Sci. 2018; 436-437.
2. Chuiko A.A. Cai Y., Li J., Yi L., Yan X., Li J. Fabricating superhydrophobic and oleophobic surface with silica nanoparticles on polymer surface. Conti J., De Coninck J., Ghazzal M.N. Design of water-repellant coating using dual scale size of hybrid silica nanoparticles on polymer surface. Appl. Surf. Sci. 2019; 471.
3. Büchel K.H., Moretto H.-H., Woditsch P., Vansant E.F., Van Der Voort P., Vrancken K.C. Colloidal Silica: Fundamentals and Applications. (Weinheim: Wiley-VCH, 2000).
4. Basic Characteristics of Aerosil. Technical Bulletin Pigments. (Weinheim: Wiley-VCH Verlag GmbH, 2006).
5.legrand A.P. Iler R.K. Chemistry of Silica Surface. (Kiyv: Naukova Dumka, 2003).
6. Legrand A.P. Basic Characteristics of Aerosil. Technical Bulletin Pigments. (Kiyv: Naukova Dumka, 2003).
7. Vansant E.F., Van Der Voort P., Vrancken K.C. Colloidal Silica: Fundamentals and Applications. (Chichester: Wiley, 1998).
8. Vansant E.F., Van Der Voort P., Vrancken K.C. Colloidal Silica: Fundamentals and Applications. (Amsterdam: Elsevier, 1995).
9. Cai Y., Li J., Li J. Fabricating superhydrophobic and oleophobic surface with silica nanoparticles modified by silanes and environment-friendly fluorinated chemicals. Appl. Surf. Sci. 2019; 469-702.
10. Cai Y., Li J., Li J. Fabricating superhydrophobic and oleophobic surface with silica nanoparticles modified by silanes and environment-friendly fluorinated chemicals. Appl. Surf. Sci. 2019; 469-702.
11. Zhu Y. Cai Y., Chen L., Guan Z. Preparation of hydrophobic antireflective SiO2 coating with deposition of PdMS from water-based SIO-PFG sol. Appl. Surf. Sci. 2018; 457-458.
12. Zhu Y., Chen L., Guan Z., Fan Z., Shi H., Yang K., Gao X., Shi G., Gong Y. Fabrication of stable biomimetic coatings using dual scale size of hybrid silica nanoparticles on polymer surface. Appl. Surf. Sci. 2019; 469-702.
13. Conti J., De Coninck J., Ghazzal M.N. Design of water-repellant coating using dual scale size of hybrid silica nanoparticles on polymer surface. Appl. Surf. Sci. 2019; 469-702.
14. Ghosh K., Roberts W.O. Collodial Silica: Fundamentals and Applications. (Boca Raton: CRC Press, 2006).
15. Bergna H.E., Roberts W.O. Collodial Silica: Fundamentals and Applications. (Boca Raton: CRC Press, 2006).

Ключевые слова: нанорефлективные, полиmericеские, силиконовые, наночастицы, поверхность, наноструктурированные, гидрофобные, гидрофильные, характеристики, адсорбция, механическая прочность, гидроуплотнение, гидрогели, гидрогель, полиметилсилоксан, характеристики, адсорбция.
Structural and adsorption features of amorphous nanosilica modified by various addition of polydimethylsiloxane

Shimizu T., Kanamori K., Maeno A., Kaji H., Nakanishi K. Transparency ethylene-bridged polymethylsiloxane as lubricants.

Sharaf M.A., Mark J.E. Modulus of randomly crosslinked polymethylsiloxane networks.

Nagappan S., Joo J., Soo S., Hong S., Sik Y. Polymethylhydrosiloxane-based organic-inorganic hybrids for amphiphobic coatings.

Gun’ko V.M., Pakhlov E.M., Goncharuk E.V., Nychi poruk Yu.M., Zarko V.I., Blitz J.P. Influence of different treatments on characteristics of nanooxide powders alone or with adsorbed polar polymers or proteins.

Leboda R., Skubiszewska-Zięba J., Leboda R., Skubiszewska-Zięba J., Goncharuk E.V., Nychiporuk Y.M., Zanko V.I., Blizt J.P. Modulus of randomly crosslinked polymethylsiloxane networks, Polymeric Materials Science and Engineering 2013.

Finiels A., Alonso B., Bousmina M., Brunel D., El Kadib A. Periodic mesoporous organosilicas derived from fluorinated polymethylsiloxane and octavinyl-POSS.

Gun’ko V.M., Turov V.V., Krupska T.V., Protsak I.S., Borysenko M.V., Pakhlov E.M. Polymethylsiloxane chemistry approach for surface modification.

Fadeev A.Y., Kazakevich Y.V. Covalently attached monolayers of oligo(dimethylsiloxane)s on silica: A siloxane chemistry approach for surface modification.

Lavrentev V.M., Barthel H., Weis J. Structure of a PDMS layer grafted onto a silica surface studied by means of DSC and solid-state NMR.

Bose B., Chatterjee A., Pal S. Synthesis of alkyl polymethylsiloxane (APMS) by condensation reaction and study of properties as lubricants.

Leboda R., Skubiszewska-Zięba J., Leboda R., Skubiszewska-Zięba J., Goncharuk E.V., Nychiporuk Y.M., Zarko V.I., Blitz J.P. Influence of different treatments on characteristics of nanooxide powders alone or with adsorbed polar polymers or proteins. Powder Technology, 2008. 187(2): 146. 

Gun’ko V.M., Turov V.V., Krupska T.V., Protsak I.S., Borysenko M.V., Pakhlov E.M. Polymethylsiloxane alone and in composition with nanosilica under various conditions. J. Colloid Interface Sci. 2019. 541: 213.

Nagappan S., Joo J., Soo S., Hong S., Sik Y. Polymethylhydrosiloxane-based organic-inorganic hybrids for amphiphobic coatings.

Gun’ko V.M., Leboda R., Skubiszewska-Zięba J., Goncharuk E.V., Nychiporuk Y.M., Zarko V.I., Blitz J.P. Influence of different treatments on characteristics of nanooxide powders alone or with adsorbed polar polymers or proteins. Powder Technology, 2008. 187(2): 146. 

Gun’ko V.M., Turov V.V., Krupska T.V., Protsak I.S., Borysenko M.V., Pakhlov E.M. Polymethylsiloxane alone and in composition with nanosilica under various conditions. J. Colloid Interface Sci. 2019. 541: 213.

Nagappan S., Joo J., Soo S., Hong S., Sik Y. Polymethylhydrosiloxane-based organic-inorganic hybrids for amphiphobic coatings.

Gun’ko V.M., Turov V.V., Krupska T.V., Protsak I.S., Borysenko M.V., Pakhlov E.M. Polymethylsiloxane alone and in composition with nanosilica under various conditions. J. Colloid Interface Sci. 2019. 541: 213.

Nagappan S., Joo J., Soo S., Hong S., Sik Y. Polymethylhydrosiloxane-based organic-inorganic hybrids for amphiphobic coatings. Compos. Interfaces. 2013. 20(1): 33.

Sharaf M.A., Mark J.E. Modulus of randomly crosslinked polymethylsiloxane networks, Polymeric Materials Science and Engineering. Proc. ACS Division of Polymeric Materials Science and Engineering. 1993. 68: 180.

Shimizu T., Kanamori K., Maeno A., Kaji H., Nakanishi K. Transparent ethylene-bridged polymethylsiloxane aerogels and aerogels with improved bending flexibility. Langmuir. 2016. 32(50): 13427.

Shimizu T., Kanamori K., Maeno A., Kaji H., Doherty C.M. Transparent ethylene-bridged polymethylsiloxane aerogels: mechanical flexibility and strength and availability for addition reaction. Langmuir. 2017. 33(18): 4543.

Zhang H., Lan C., Ana F., Teixeira L., Michaela S. Water-based freeze casting: Adjusting hydrophobic polymethylsiloxane for obtaining hierarchically ordered porous SiOC. J. Am. Ceram. Soc. 2017. 100(5): 1907.

Zu G., Shimizu T., Kanamori K., Zhu Y., Maeno A., Kaji H., Shen J., Nakanishi K. Transparent, super flexible doubly cross-linked polyvinyl/polymethylsiloxane aerogel superinsulators via ambient pressure drying. ACS Nano. 2018. 12(1): 521.

ISSN 2079-1704. ХФТИ 2019. Т. 10. № 3 217
42. Michurina S.V., Ischenko I.Y., Arkhipov S.A., Klimontov V.V., CherepanovaM.A., Korolev M.A., Rachkovskaya L.N., Zav E.L., Konenkov V.I. Melatonin – aluminum oxide – polydimethylsiloxane complex on apoptosis of liver cells in a model of obesity and type 2 diabetes mellitus. *Bulletin of Experimental Biology and Medicine.* 2017. 164: 165.

43. Gun’ko V.M., Turov V.V., Pakhlov E.M., Matkovsky A.K., Krupska T.V., Kartel M.T., Charmas B. Blends of amorphous/crystalline nanoalumina and hydrophobic amorphous nanosilica. *J. Non-Cryst. Solids.* 2018. 500: 351.

44. Gun’ko V.M., Turov V.V., Pakhlov E.M., Krupska T.V., Borysenko M.V., Kartel M.T., Charmas B. Water interactions with hydrophobic versus hydrophilic nanosilica. *Langmuir.* 2018. 34(12): 12145.

45. Gun’ko V.M., Turov V.V., Krupska T.V., Pakhlov E.M. Behavior of water and methane bound to hydrophilic and hydrophobic nanosilicas and their mixture. *Chem. Phys. Lett.* 2017. 690: 25.

46. Turov V.V., Gun’ko V.M., Pakhlov E.M., Krupska T.V., Tsapko M.D., Charmas B., Kartel M.T. Influence of hydrophobic nanosilica and hydrophobic medium on water bound in hydrophilic components of complex systems. *Colloids Surf. A.* 2018. 552: 39.

47. Gregg S.J., Sing K.S.W. *Adsorption, Surface Area and Porosity.* (London: Academic Press, 1982).

48. Adamson A.W., Gast A.P. *Physical Chemistry of Surface.* 6th edition. (New York: Wiley, 1997).

49. Neimark A.V., Ravikovitch P.I. Capillary condensation in MMS and pore structure characterization. *Microporous Mesoporous Mater.* 2001. 44/45: 697.

50. Gun’ko V.M. Composite materials: textural characteristics. *Appl. Surf. Sci.* 2014. 307: 444.

51. Strange J.H., Rahman M., Smith E.G. Characterization of porous solids by NMR. *Phys. Rev. Lett.* 1993. 71: 3589.

52. Mitchell J., Webber J.B.W., Strange J.H. Nuclear magnetic resonance cryoporometry. *Phys. Rep.* 2008. 461: 1.

53. Petrov O.V., Furó I. NMR cryoporometry: Principles, applications and potential. *Prog. Nucl. Magn. Reson. Spectros.* 2009. 54(2): 97.

54. Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Scalmani G., Barone V., Mennucci B., Petersson G.A., Nakatsuji H., Caricato M., Li X., Hratchian H.P., Izmaylov A.F., Bloino J., Zheng G., Sonnenberg J.L., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery J.A., Jr., Peralta J.E., Ogliaro F., Bearpark M., Heyd J.J., Brothers E., Kudin K.N., Staroverov V.N., Keith T., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J.C., Iyengar S.S., Tomasi J., Cioslowski J., Fox D.J.

55. Stewart J.J.P. *MOPAC2016,* Stewart Computational Chemistry. 2017. http://OpenMOPAC.net.

56. Stewart J.J.P. Optimization of parameters for semiempirical methods VI: more modifications to the NDDO approximations and re-optimization of parameters. *J. Mol. Model.* 2013. 19(1): 1.

57. Zhurko G.A., Zhurko D.A. Chemcraft (version 1.8, build b536a). 2017. http://www.chemcraftprog.com.

58. Hanwell M.D., Curtis D.E., Lonie D.C., Vandermeersch T., Zurek E., Hutchison G.R. Avogadro: an advanced semantic chemical editor, visualization, and analysis platform. *J. Chem. Inform.* 2013. 4(1): 17.

59. Emsley J.W., Feeney J., Sutcliffe L.H. *High Resolution Nuclear Magnetic Resonance Spectroscopy.* (Oxford: Pergamon Press, 1965).

60. Chaplin M. Water structure and science. 2018. http://www1.lsbu.ac.uk/water/.

61. Gun’ko V.M., Turov V.V., Pakhlov E.M., Krupska T.V., Kartel M.T., Charmas B. Effect of water content on the characteristics of hydro-compact ed nanosilica. *Appl. Surf. Sci.* 2018. 459: 171.

62. Turov V.V., Geraschenko I.I., Krupska T.V., Suvorova L. *Nanochemistry in solution of problems of exo- and endo-ecology.* (Stavropol: Zebra, 2017). [in Russian].

63. Mikhail’ev Yu.A., Guseva L.N., Davydov E.Ya., Ershov Yu.A. The hydration of hydrophobic substances. *Russ. J. Phys. Chem.* 2007. 81(12): 1897.

64. Yaminsky V.V., Vogler E.A. Hydrophobic hydration. *Current Opinion in Colloid & Interface Science.* 2001. 6(4): 342.

65. Widom B., Bhimalapuram P., Koga K. The hydrophobic effect. *Phys. Chem. Chem. Phys.* 2003. 5(15): 3085.

Received 04.04.2019, accepted 20.08.2019