The role of free silanol groups of nanosilica surface on the interaction with poly(vinyl pyrrolidone)

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In this work, the role of the number of free silanol groups at the nanosilica surface (specific surface area $S_{BET} = 250$ m^2/g, initial amount of silanols $\alpha_{OH} = 0.60$-0.62 mmol/g) was analyzed in interaction with poly(vinyl pyrrolidone) (PVP) vs. the degree (Θ_{TMS}) of silica hydrophobization by hexamethyldisilazane at 100°C. The values of Θ_{TMS} were found 0.07, 0.42, 0.67, 0.81, 0.82, and 1.0. Adsorption of PVP onto the nanosilica surface was carried out from water and water-ethanol (1:1) solutions of the polymer. It was found that free silanol groups play a crucial role in the adsorption of poly(vinyl pyrrolidone). The value of the maximal adsorption (monolayer capacity) on completely hydrophobic nanosilica surface is approximately lower than that for unmodified nanosilica by a factor of about 6.5.

Keywords: Nanosilica, Silanol groups, Hydrophobization, Hexamethyldisilazane, Poly(vinyl pyrrolidone) adsorption.

1. INTRODUCTION

Fumed high-disperse nano-scaled silica has been found a quite appropriate for creating a variety of materials with specified properties due to its characteristically large specific surface area, small size of initial nanoparticles (~10 nm), and chemical structure of a silica surface [1]. Nanosilica is widely used in various industries as a filler of polymer compositions in the manufacture of varnishes and paints, certain types of rubber, thickener of oils, etc. [1], as well as a sorbent in medicine [2]. Medicinal preparations for sorption detoxication based on nanosilica have proved to be an effective tool in the complex treatment of surgical, infectious, oncological and some other diseases [3].

Immobilization of bio-active compounds (BAC) on a surface of nanosilica makes it possible to obtain complex medicines with new properties with respect to the nature and range of action. Some of these properties, such as pharmacokinetics, are largely determined by the structure of the surface adsorbed layer of BAC, which can be uniform or to consist of individual clusters of the molecules or ions [4].

At the same time, there seems to be no general point of view on the structure of the hydrated surface layer of nanosilica. There are different views on the nature of active surface sites with silanol groups (e.g., free or hydrogen-bound, alone or twin or vicinal) determining the sorption and chemisorption properties of silica [5].

It is obvious that understanding a role of certain active sites in surface processes is possible by changing their concentration and observing how this affects the phenomenon. Therefore, controlled replacement of silanol groups by trimethylsilyl ones using chemical reactions allows one to determine the modification effect on adsorption of test compounds of both low- and high-molecular weight.

Free silanol groups are the main active sites at the surface of any silica [5-9]. These groups appear in the infrared (IR) spectra as a narrow intense absorption band at 3748-3750 cm^{-1}. These groups can participate in the formation of strong hydrogen bonds and, therefore, to dominate on the adsorption properties of silica. The participation of hydrogen-bound silanol groups, which correspond to IR adsorption bands with maximum of ~3500 and 3660-3680 cm^{-1} is a subject of discussion [5-9]. Additionally, van der Waals forces can play an important role in the adsorption interactions at the surface of silica, in particular, in the adsorption of nonpolar compounds and polymers. Contribution of the

above mentioned factors to the adsorption of macromolecules is assessed differently by different authors. Surface chemistry researchers [5-9] assume that the formation of hydrogen bonds are the main factor, but researchers working on the adsorption of polymers believe that dispersive interactions are more important [10, 11]. Therefore, the aim of this study was to determine the role of free surface silanol groups of fumed nanosilica in the adsorption interaction with poly(vinyl pyrrolidone) (PVP). To that aim, the content of free silanol groups was varied by successive substitution at trimethylsilyl by reacting with hexamethyldisilazane (HMDS) flowing according to the scheme:

$$2 \equiv SiOH + (CH_3)_3Si\text{-}NH\text{-}Si(CH_3)_3 \rightarrow 2 \equiv SiOSi(CH_3)_3 + NH_3$$

2. MATERIALS AND METHODS

2.1. Materials

Fumed silica ("Orisil", Kalush, Ukraine, specific surface area $S_{BET} = 250$ m^2/g, bulk density of ~0.05 g/cm^3, and concentration of free silanol groups (α_{OH}) 0.61 ± 0.01 mmol/g) was used as unmodified sample. Note that 1 g of this nanosilica contains approximately 10^{18} particles of 10-12 nm in size.

Hexamethyldisilazane (HMDS) ("Siliconpolymer", Zaporozhye, Ukraine, degree of purity "h") was used as a modifier of nanosilica. Poly(vinyl pyrrolidone) (Biopharma, Kiev, pharmaceutical purity) $(-CH_2CH(R)-)_n$, where $R = NC_4H_6O$, $n \approx 100$, molecular weight of 12600 ± 2700, was used as received.

2.2. Chemical modification of silica.

Interaction of silica with HMDS vapour was carried out at 120°C in a glass reactor equipped with an impeller (400-500 rpm). Dropwise addition of HMDS was performed onto intensely mixed nanosilica at fluidized state. The reaction time was 3 hours. Then, to remove the by-products, the reactor was purged with air at 120°C for 30 min. The degree of nanosilica surface modification with the TMS groups depends on the amount of HMDS introduced into the reactor [12]. Hydrophobized silica samples were prepared at $\Theta_{TMS} = 0.07, 0.42, 0.67, 0.81, 0.82,$ and 1.0.

2.3. IR spectroscopy

The infrared (IR) spectra were recorded using with a Thermo Nicolet (Nicolet Instrument Corporation, USA) spectrometer. Samples of investigated silica were pressed into plates measuring 8×28 mm and weighing 20 ±0.5 mg in a special press mold.

The degree of silica modification by HMDS was controlled using IR spectroscopy to estimate changes in the intensity of the bands of free silanols at 3750 cm^{-1} and the C–H bonds in TMS at 2800-3000 cm^{-1}. The value of Θ_{TMS} was determined from the ratio of the optical densities (D) of the absorption bands at 3750 cm^{-1} in the modified (D) and initial (D$_0$) silicas by the formula:

$$\Theta_{TMS} = 1 - D/D_0 \qquad (1)$$

where $D = \lg (100–I_0)/(100–I)$, and I_0 and I are the intensities of the IR baseline and the band at 3750 cm^{-1} [13].

2.4. Textural characteristics

The specific surface area, S_{BET}, was calculated according to the standard BET method [14]. The pore volume, V_p (estimated at p/p$_0$ ≈ 0.98, where p and p$_0$ denote the equilibrium and saturation pressures of nitrogen, respectively) was determined using nitrogen adsorption/desorption isotherms recorded at 77.4 K using a Micromeritics ASAP 2405N adsorption analyzer.

2.5. Adsorption of PVP

Adsorption of PVP on a surface of the initial silica was studied using aqueous and water-ethanol (1:1 v/v) solutions of PVP. In the case of strongly hydrophobized samples, the polymer was adsorbed only from water-ethanol solutions [15].

The adsorption was carried out under static conditions at 25 ± 0.1°C adding 16 ± 0.05 cm^3 of a PVP solution of various concentrations into eight flasks and then 200 mg of silica was added and the resulting suspension was mixed. After 1 hour of contact, the suspension was centrifuged at 8000 rpm for 30 min. The silica studied is composed of nonporous nanoparticles. Therefore, this time is sufficient to establish sorption equilibrium [2]. The adsorption value of PVP (A) was calculated by the formula:

$$A = (C_0 - C_{eq})V/m \tag{2}$$

where C_0 and C_{eq} (g/cm^3) are the initial and equilibrium concentrations of PVP in solutions, respectively, m is the silica weight (g); V is the volume of the solution (cm^3). The equilibrium concentration of PVP was determined by the photocolorimetric method using iodine [16]. Calibration graphs were built separately for aqueous and water-alcohol solutions.

2.6. Impregnation

The impregnation of unmodified and modified silica powders by polymer solution was used to study the surface state of samples modified with different amounts of poly(vinyl pyrrolidone). A water-ethanol mixture was used as solvent. The silica content in the suspensions was 10 wt.%, and the polymer concentration was varied from 20 to 175 mg per 1 g of silica.

3. RESULTS AND DISCUSSION

The hydration (bound water) – hydroxyl (SiOH) layer on a silica surface is characterized by four IR absorption bands related to the O–H stretching vibrations at 3300-3350, ~3500, 3660-3680, and 3750 cm^{-1} (Fig. 1) [5-9].
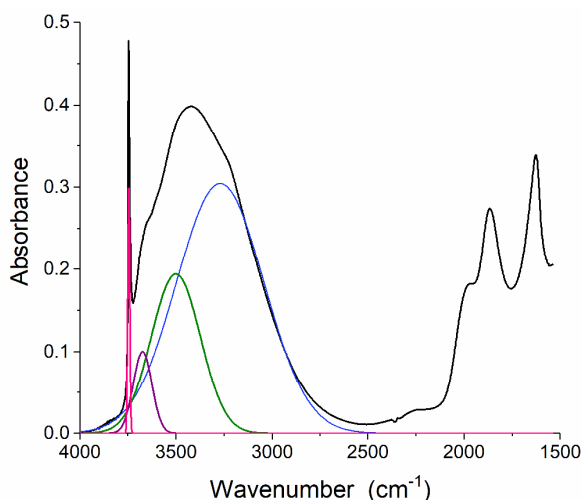

Fig. 1. IR spectrum of degassed nanosilica with decomposition of the bands of the O-H stretching vibrations.

Interpretation of two bands of the O–H stretching vibrations (ν_{OH}) is common accepted and a narrow band at 3750 cm^{-1} is attributed to free silanols and a broad band at 3250 cm^{-1} is due to adsorbed water. However, there are different opinions on the bands at 3680 and 3500 cm^{-1}. A band at 3500 cm^{-1} could be assigned to closely located (~ 0.3 nm) vicinal or other silanols with the hydrogen bonds. Silanols located in places difficultly accessible for adsorbates, e.g. in shallow pores, give a band at 3680 cm^{-1} [5, 6]. A role of hydrogen-bonded silanols in adsorption and chemisorption processes remains controversial. Some authors assumed that these groups do not take part in adsorption and chemical processes at a silica surface [7]. However, others assumed [17] that both alone free and vicinal OH groups can interact with adsorbed molecules.

3.1. Interaction with HMDS

In the case of gas-phase modification of nanosilica with hexamethyldisilazane, the infrared spectra of samples at different values of Θ_{TMS} (Fig. 2) show a gradual decrease in intensity of three ν_{OH} bands at 3750, 3500, and 3250 cm^{-1} is observed. However, the band at 3680 cm^{-1} does not change the intensity, but there is a small shift toward smaller values of ν_{OH} with increasing Θ_{TMS}. Thus, different silanols with one exception of poorly accessible ones (with a band at 3680 cm^{-1}) at a nanosilica surface can participate in the interaction with HMDS.
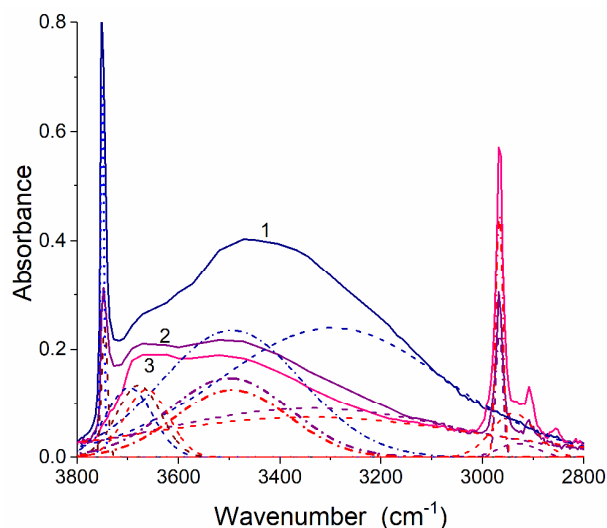

Fig. 2. IR spectra of silicas (1) initial and hydrophobized at Θ_{TMS} = (2) 0.42 (2) and (3) 1.0.

The physicochemical properties of silica depend not only on the chemical nature of the surface, but that are affected by the value of the specific surface area (S_{BET}). Therefore, it is important to analyze changes in the value of S_{BET} due to the surface modification. For this purpose, the specific surface area of the initial as well as partially and completely modified nanosilica was measured (Fig. 3).
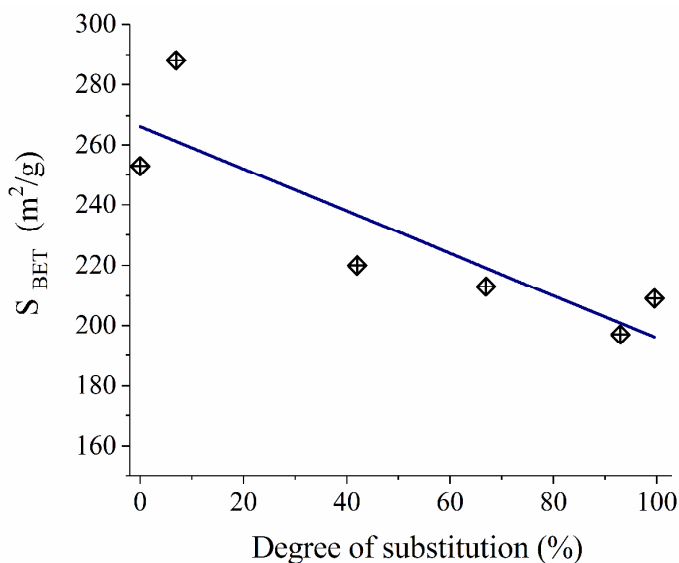

Fig. 3. Dependence of the specific surface area of nanosilica on the degree of substitution of silanol groups on trimethylsilyl which was estimated from IR spectra. Here and in Figures 4a, 5, 6a and 7 the shown lines are special fittings of the linear spline-interpolation to the experimental points.

Modification of silica can lead to a decrease in the value of the specific surface area determined by low-temperature adsorption of nitrogen [18]. For the initial nanosilica at $S_{BET} = 253$ m^2/g, the average particle size is 10.9 nm. If it is assumed that the size of a trimethylsilyl group is approximately 0.5 nm, completely modified nanosilica particle size increases to 11.9 nm that results in a decrease in the specific surface area. Thus, a decrease in the S_{BET} value is ca. 20% for completely modified nanosilica with the TMS groups (Fig. 3).

3.2. Nanosilica interaction with PVP

The adsorption of polymers on a solid surface depends on the properties of both a solute and a solvent and the latter is quantitatively characterized by the value of the second virial coefficient [10]. This value

could be estimated using viscometry; however, in this case, instead of the virial coefficient a constant k could be determined with an equation:

$$\eta_{spec}/C = \eta + k\eta^2 C \tag{3}$$

where η is the viscosity, and C is the solute concentration.

The value of k characterizing interaction of a solute (e.g. PVP) with a solvent increases for poor solvents. To determine the viscosity, the PVP solutions were equilibrated at room temperature for 24 h, then it was thermostated at $25 \pm 0.1°C$ for 15 min, and time (τ) of flowing-out of the solution from a viscometer was measured. The relative viscosity was calculated $\eta_{rel} = \tau_{sol}/\tau_{solv}$, the specific viscosity $\eta_{spec} = \eta_{rel} - 1$ was used to plot the dependence η_{spec}/C vs. C. It was used to estimate the values of η and $k\eta^2$ and then k. This gives $k = 0.78$ and 0.25 for water and water/ethanol mixture, respectively. Thus, the latter is a better solvent for PVP than water. This difference can lead to difference in the PVP adsorption onto nanosilica from aqueous and water/ethanol solutions.

The PVP adsorption on a surface of the initial silica from aqueous and water/ethanol solutions (Fig. 4a) well described by the Langmuir equation is better from the aqueous solution because water is a worse solvent than the mixture. This leads to a smaller value of the desolvation energy upon the PVP adsorption from the water solution and, therefore, greater values of $|\Delta G|$ in comparison with the adsorption from the water/ethanol solution (Fig. 4b).
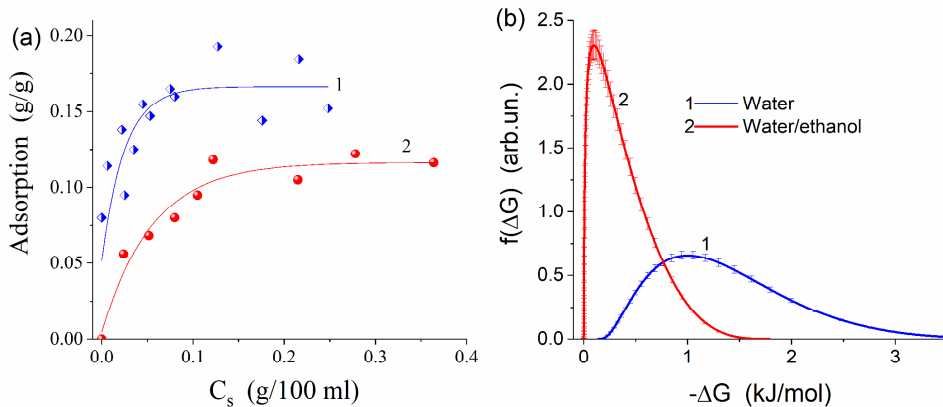

Fig. 4. (a) PVP adsorption isotherms on the initial nanosilica from aqueous (1) and water/ethanol solution (2); and (b) the distribution function of the Gibbs free energy of adsorption (calculated using the right term of the Langmuir equation as the kernel of the integral equation [V.M. Gun'ko, V.V. Turov, Nuclear Magnetic Resonance Studies of Interfacial Phenomena, CRC Press, Boca Raton, 2013]) of PVP onto nanosilica from aqueous (1) and water/ethanol (2) solutions.

The values of monolayer capacity for PVP is 170 mg/g and 130 mg/g for water and water/ethanol solutions, respectively. Additionally, desorption of PVP is better in the water/ethanol medium (Fig. 5).
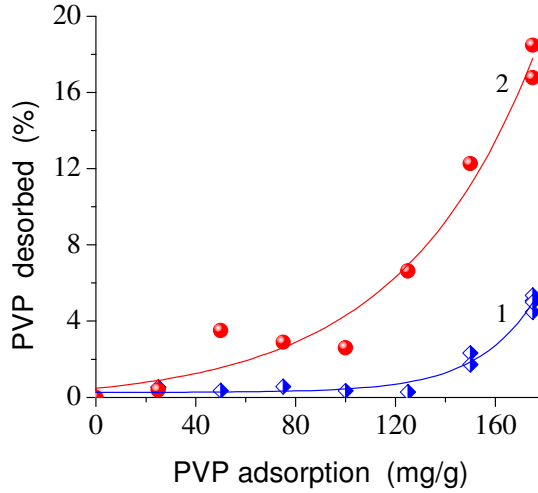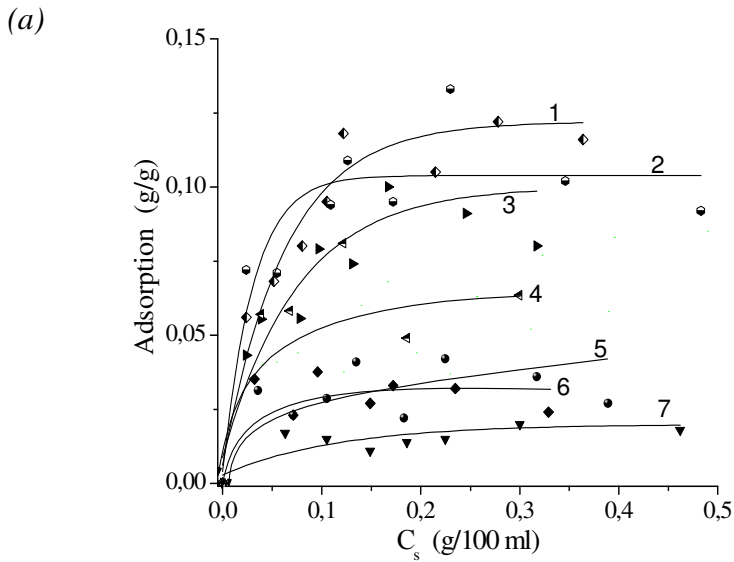

Fig. 5. Dependence of PVP desorption from the nanosilica surface vs. the adsorbed amount of PVP in aqueous (1) and water/ethanol media (2).
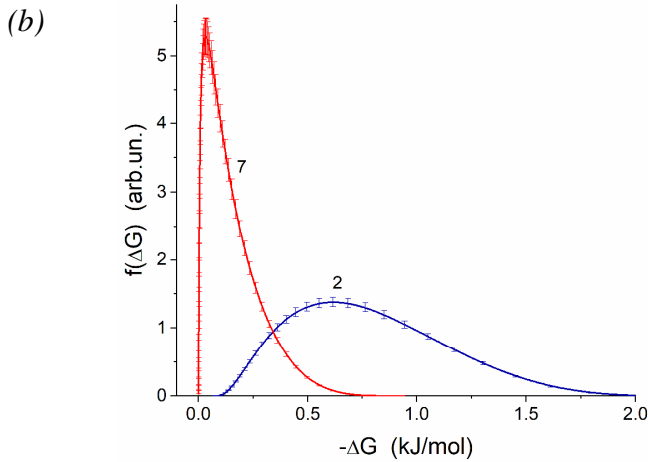
(b)

Fig. 6. (a) Isotherms of PVP adsorption from a water-ethanol solution on the surface of nanosilica: hydrophilic (1) and with the degree of hydrophobization 7 (2), 42 (3), 67 (4), 81 (5), 82 (6) and 100% (7); and (b) the distribution function of the Gibbs free energy of adsorption of PVP onto modified nanosilica from water/ethanol solution at 7% (curve 2) and 100 % (7) hydrophobization.

Increase in the degree of hydrophobization of nanosilica leads to a decrease in PVP adsorption (Fig. 6a), and the maximum adsorption decreases practically linearly (Fig. 7). The content of the PVP monolayer on fully modified silica is approximately 6.5 times smaller than that for the unmodified silica (20 and 130 mg/g, respectively). There is a significant difference in the f(ΔG) curves for modified silicas with minimal and maximal degree of hydrophobization, as well as for unmodified silica (Figs. 4b and 6b).
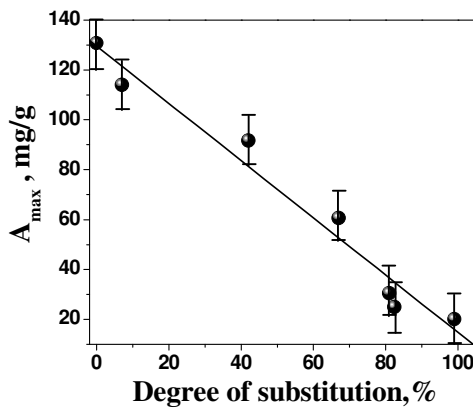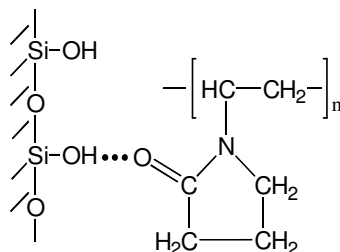

Fig. 7. Dependence of maximum PVP adsorption on the degree of hydrophobization of the silica surface.

PVP adsorbed onto the surface of hydroxylated disperse silica due to the formation of hydrogen bonds between the oxygen atoms of the carbonyl groups of the polymer and free silanol groups [19-21]:

The energy of these bonds, estimated from the IR spectra using the shift of the absorption band of free silanol groups at 3750 cm^{-1}, is 48-50 kJ/mol [20]. Therefore, the substitution of silanol groups for trimethylsilyl groups can lead to a significant decrease in the adsorption energy and, therefore, in the adsorption values of PVP.

3.3. IR spectroscopy study of PVP interaction with silica surface.

The IR spectra of PVP sorbed on the surface of the unmodified and modified silica are practically the same (Figs. 8-11). All of them contain absorption bands characterizing the C=O stretching vibrations of the amide group at 1700 cm^{-1}, the valence and deformation vibrations of C–H in the ranges of 1300-1500 and 2800-3000 cm^{-1}, respectively. The difference between the spectra of different samples is in intensity of the band at 3750 cm^{-1}.

If a PVP monolayer (175 mg/g) is formed on the unmodified silica, practically all free silanol groups participate in interactions with adsorbed molecules since the band at 3750 cm^{-1} disappears (Fig. 8). Partial substitution of silanols by TMS groups affects the accessibility of silanols for PVP molecules. If PVP is adsorbed in the amount sufficient to cover a hydrophilic part of the surface that not all free silanol groups interact with the PVP and adsorbed water molecules (Figs. 9 and 10).
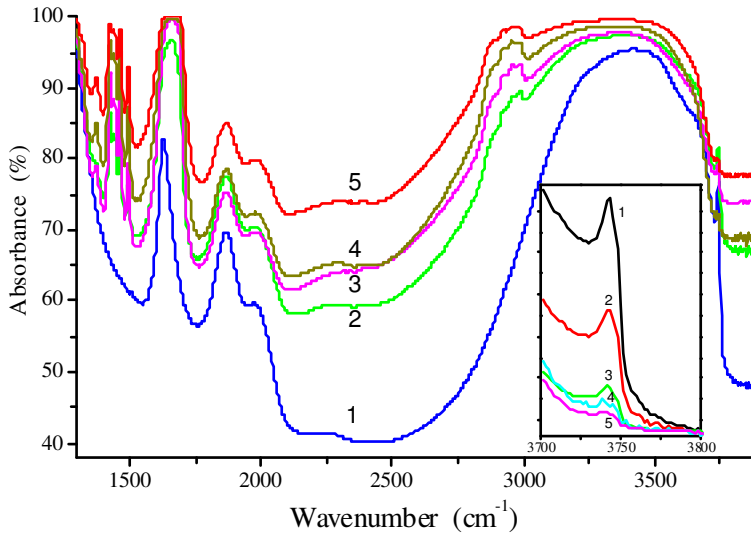
Fig. 8. IR spectra of nanosilica (1) after adsorption of 50 (2), 100 (3), 150 (4), and 175 mg (5) of PVP per gram of dry silica from the water/ethanol solution.
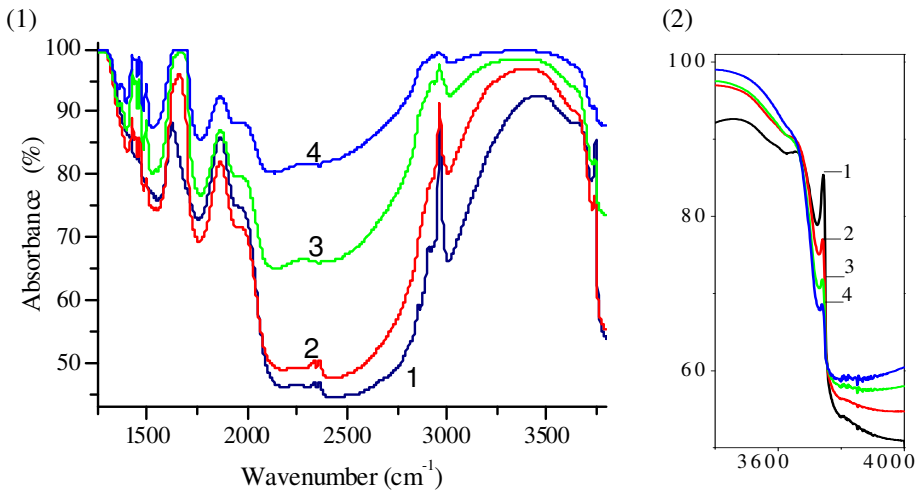

Fig. 9. IR spectra of nanosilica with a degree of hydrophobization of 42% (1) after adsorption from a water-alcohol solution of 20 (2), 60 (3) and 100 mg/g PVP (4).
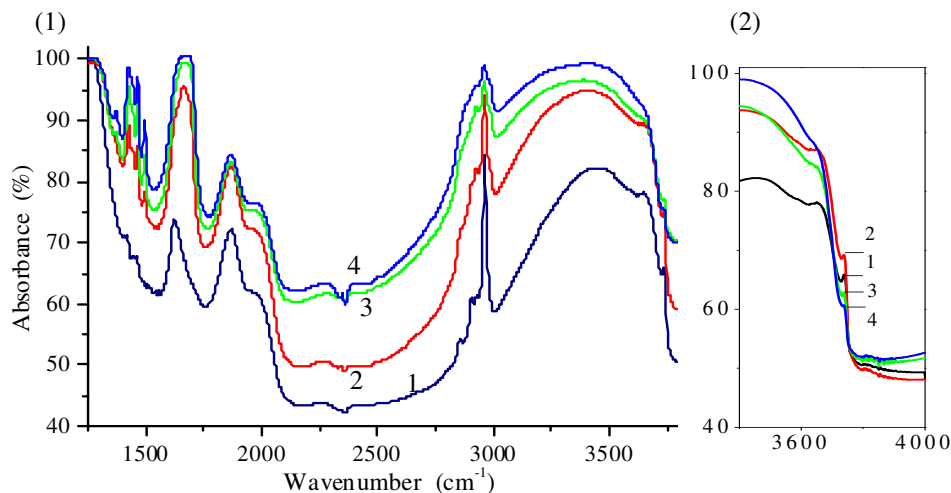
Fig. 10. IR spectra of nanosilica with a degree of hydrophobization of 67% (1) after adsorption from a water-alcohol solution of 20 (2), 60 (3) and 100 mg/g PVP (4).

If 175 mg/g PVP is enough to interact with all free silanol groups of unmodified silica, that for 42% modified silica, one could expect that 100 mg/g is enough to interact with all silanols (if PVP is preferably bound to hydrophilic patches). Similarly, for 67% hydrophobization, 60 mg/g could be enough. However, at these concentrations of PVP, the band at 3750 cm^{-1} is still present in the IR spectra (Figs. 8-10).
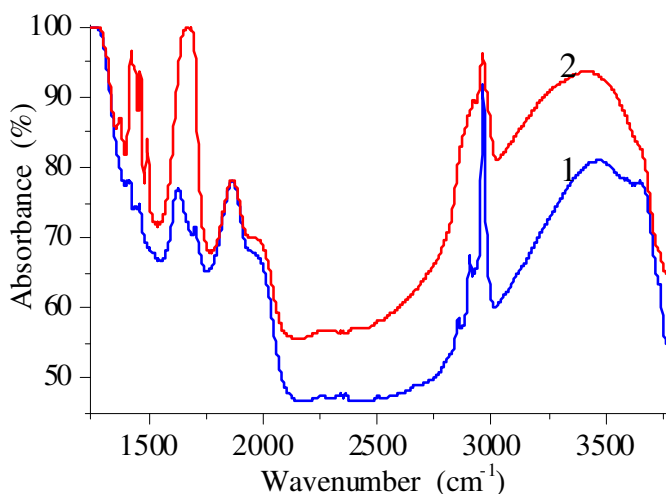

Fig. 11. IR spectra of fully hydrophobized nanosilica (1) and after the PVP adsorption from a water-ethanol solution of 100 mg/g PVP (2).

These features of the IR spectra could be explained by several factors: (i) the accessibility of remained silanols at a surface of partially modified silica is lower due to steric factors than that for unmodified silica; (ii) PVP having restricted flexibility of the chain and interacting with the TMS groups (despite decreased energy of interactions, Figs. 4b and 6b) screening the surface silanols that results in incomplete coverage of the hydrophilic patches of the surface by PVP.

Upon the PVP adsorption onto fully hydrophobized silica, the IR spectrum is the sum of the spectra of the components (Fig. 11). Therefore, certain changes are observed in the range of the C–H stretching vibrations. However, the high intensity of the bands ~ 1650 cm^{-1}, 1300-1500 and 2800-3000 cm^{-1} indicate that PVP is in a highly disperse state. This means that PVP well distributed over the surface of modified nanosilica without forming large polymer particles.

4. CONCLUSIONS

Free silanol groups play an important role in the adsorption of poly(vinyl pyrrolidone) on the surface of nanosilica with respect to both the adsorption energy and structure of the adsorbed layer. From the ratio of maximum adsorption of PVP to fully hydroxylated and hydrophobic silica, it can be concluded that the contribution of van der Waals forces to the interaction of the surface with PVP causes relatively small changes in the Gibbs free energy of the adsorption, but they are driving forces on the control of the structure of the PVP adsorption layer, i.e. the macromolecules are well distributed onto the surface of completely modified nanosilica despite lower interaction energy of PVP with the TMS groups.

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