

# Amino acids adsorption in differently aged and concentrated aqueous suspensions of ZnO and TiO<sub>2</sub> nanoparticles

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**Abstract.** Amino acids may be effectively used for preventing aggregation of engineered nanoparticles (NPs) in aqueous suspensions. This paper is primarily focused on the influence of exposure duration and particles content on adsorption coefficient (Ads) for ZnO and TiO<sub>2</sub> nanoparticles with an average size of 40-60 nm exposed to 2M aqueous solutions of glycine and L-glutamic acid. The value of Ads was estimated from surfactant concentration related to the intensity of infrared peak spectroscopy at 1300-1400 cm<sup>-1</sup>. It has been shown that in more concentrated suspensions (0.08-0.12 g/mL) Ads has ±5% fluctuation in measurement error interval, whereas in less concentrated systems (0.02-0.04 g/mL) 3...20 h exposure of NPs may result in slight desorption of surfactant as shown for ZnO NPs or total desorption of surfactant as shown for TiO<sub>2</sub> NPs in glycine solutions. Six times decrease of 0.02 g/mL NPs concentration leads to Ads augmentation by 3-4 and 1.5-6 times, respectively, on ZnO and TiO<sub>2</sub> nanoparticles. From a methodological view point, it has been concluded that in order to provide effective comparative study of NPs adsorption properties it is not reasonable to concentrate the NPs suspension more than 0.04 g/mL and it is better to expose them during 3 h in order to avoid surfactant desorption.

## 1. Introduction

Global market of metal oxides nanoparticles (NPs), presently valued at 1.8 billion US dollars, will soar till 10.4% of the compound annual growth rate to surpass 5 billion US dollars mark by the end of 2026 [1]. Titanium dioxide (TiO<sub>2</sub>) and zinc oxide (ZnO) NPs are maximally produced due to a wide range of applications. TiO<sub>2</sub> NPs are widely used as a pigment, thickener and absorber of ultraviolet radiation in sunscreens, in paints and varnishes, in pharmaceutical and cosmetic industries, in medicine [2-3] and as a photocatalytic component in environmental technologies and energetics [4]. Zinc oxide (ZnO) NPs are used as components for varnishes, whitewashes and paints, cosmetics and medicaments [5], gas- and bio-sensors [6], optical and electrical devices, solar batteries [7], antibacterial agents and drug delivery systems [8]. Although NPs are applied in the form of aqueous dispersion in many applications



[4, 7-9], preparation of dispersions from engineered NPs is still quite difficult, since NPs tend to inconvertible aggregation due to their high surface energy and small size [10].

In practice, only the addition of surfactants makes it possible to maintain NPs stability for a long time [11]. Although, there are numerous papers on the use of surfactants for NPs synthesis [12], the selection of surfactants for industrial particles is still embarrassing. The literature is overflowed by research methods of physical and chemical nature of adsorption. The bonding and the structure of amino acid monolayers deposited onto metal or metal oxide surfaces can be experimentally investigated with modern surface science tools including electron and optical spectroscopic methods in ultrahigh vacuum environments [13],  $^1\text{H}$  NMR spectroscopy [14], sum frequency generation vibrational spectroscopy [15], attenuated total reflection IR [16] or theoretically predicted by molecular-dynamics simulations [17] in the presence of water. These authors found that weak adsorbate-substrate interactions involving both carboxylate and ammonium moieties were possible. Langel and Koppen used a similar approach to study the adsorption of amino acids adsorbed on the anatase- $\text{TiO}_2$  (101) and (001) surfaces, and the rutile- $\text{TiO}_2$  (110) surface [17-18]. There are data showing that amino acids, as lysine [19], glycine [20], cysteine [21], glutamic acids [22], aspartic acids [19], tryptophan [23], tyrosine [24] may be potentially absorbed by engineered NPs. For instance, glutamic and aspartic acids adsorbed to  $\text{TiO}_2$  particles ( $0.8 \cdot 10^{-3}$  g/mL) from aqueous solutions [25]. Glycine adsorbed to the amorphous spherical  $\text{TiO}_2$  NPs [16] compared to [26] where glycine was not adsorbed onto the rutile- $\text{TiO}_2$  NPs ( $0.4 \cdot 10^{-3}$  g/mL) in  $\text{H}_2\text{O}$  solvents.

In spite of deep understanding of adsorption process, resulted data have been obtained under different experimental conditions and cannot be compared. Moreover, applied research methods can be hardly introduced into industry-scale practice for express estimation of adsorption effectiveness on NPs.

In this paper, we offer a simple express method for determining the adsorption coefficient of engineered NPs in aqueous solutions of amino acids; that would allow quickly assessing the effectiveness of adsorption as the function of particles concentration and exposure time.

## 2. Experimental part

### 2.1. Nanoparticles and surfactants

In the present study, we used two types of engineered plasmachemical nanoparticles: ZnO and  $\text{TiO}_2$ , purchased from Nanostructured & Amorphous Materials Inc. (USA). The powders were white in colour.

Two aliphatic amino acids were examined as stabilizers of particles: aminoacetic acid (Gly, glycine,  $\text{NH}_2\text{-CH}_2\text{-COOH}$ , CAS 56-40-6) and glutamic acid (Glut, L-glutamic,  $\text{C}_5\text{H}_9\text{NO}_4$ , CAS 56-85-9) produced by Sigma Aldrich.

### 2.2. Determination of dry particles morphology

Transmission electron microscopy (TEM) was performed using JEM 2100F microscope (Jeol, Japan, point resolution 2.3 Å, lines 1.4 Å) to determine the morphology of particles and their aggregates. The particles were transferred onto a copper grids coated with carbon prior to be irradiated in vacuum with electrons from a  $\text{LaB}_6$  emitter at the voltage of 50...200 keV.

Specific surface area (SSA) of powders was determined by low-temperature nitrogen adsorption (Brunauer-Emmett-Teller, BET) method using SorbiPrep (META, Russia). The assay was repeated at least three times, and the measurement error was  $0.2 \text{ m}^2/\text{g}$ . The resulting SSA was used to calculate the average surface diameter, assuming that nanoparticles were spherical and had equal diameter, according to the experimental formula:

$$d = \frac{6}{\rho \cdot S} \quad (1)$$

### 2.3. Preparation of surfactant solutions

Surfactant solutions with the concentration of 2M were prepared using distilled water (pH=6.11±0.2, conductivity 0.2 μC, distiller D-30938, Gesellschaft Labortechnik mbH) at the temperature of 22±2°C. All samples were taken using analytical weights AGN-200 (Axis, Poland, measurement error ±0.0001 g). Glutamic acid solution was basified using NaOH in a ratio of 1:1 mole until complete dissolution. The pH value was monitored by a pH meter Expert-001 (LLC "Electronics-Expert", Russia). All solutions were stored no more than three days.

### 2.4. Preparation of nanoparticle suspensions

Suspensions with particle concentration of 0.02...0.12 g/mL were prepared by direct adding of dry nanopowder to prepared surfactant solution (5 mL) followed by stirring in a magnetic stirrer (Heidolph MR Hei-Tec, 700 rpm, 5×10 mm magnet) for 20 h in closed plastic container at 22±2°C. After different aging time 2.5 mL of suspension was centrifuged during 60 minutes at a speed of 5500 rpm using centrifuge HETTICH EBA 20 (Germany). Supernatant was used to determine the adsorption coefficient.

### 2.5. Determination of the adsorption coefficient (*Ads*)

IR spectra of supernatant (layer of 0.005...0.1 mm thickness) was measured using Thermo Nicolet 380 IR Fourier spectrometer in the wavenumber range of 4000 to 400 cm<sup>-1</sup>.

It is known that in a certain range of surfactant concentrations, the height of the peaks on the IR spectrum can be correlated with the acid concentration [27]. However, in water-based solution, the most visible peaks corresponding to the carboxyl groups (1600 cm<sup>-1</sup>) [28] coincide with peaks demonstrating the vibrations of OH-groups in water (1580-1750 cm<sup>-1</sup>) [28]. Therefore, Hidberg *et al.* [29] have used another water structure when studying the adsorption of citric acid on alumina particles. The intense adsorption spectrums of amino acids are based at 1328, 1409 and 1506 cm<sup>-1</sup> (for glycine) and 1344, 1400 and 1550 cm<sup>-1</sup> (for glutamine) which correlate, respectively, with ρ(NH<sub>3</sub>) (rocking), τ(NH<sub>2</sub>) (twisting), and to ρ(NH<sub>3</sub>) and δ(NH<sub>2</sub>) (scissoring) vibrations of amino groups that do not coincide with the absorption bands of water.

To estimate the efficiency of amino acid adsorption on the particle surface, we compared the surfactant concentration in exposed solution with initial acid content by determining the height of IR spectrum peak depending on the amino acid concentration in solution. In the work we analyzed peaks at 1330.71 cm<sup>-1</sup> and 1400.11 cm<sup>-1</sup> for glycine and glutamic, respectively. The adsorption coefficient (*Ads*, M/m<sup>2</sup>, *Ads*<sub>Gly</sub> and *Ads*<sub>Glut</sub> – *Ads* value of glycine and glutamic, respectively) was calculated using the formula (2):

$$Ads = \frac{(C_i - C_f)}{1000 \cdot m_{NP} \cdot S}, \quad (2)$$

where *C<sub>i</sub>* was surfactant concentration in the initial solution, mol/L; *C<sub>f</sub>* – surfactant concentration in supernatant, mol/L; *m<sub>NP</sub>* – concentration of nanoparticles, g/mL; *S* – specific surface area of particles, m<sup>2</sup>/g.

## 3. Results and discussion

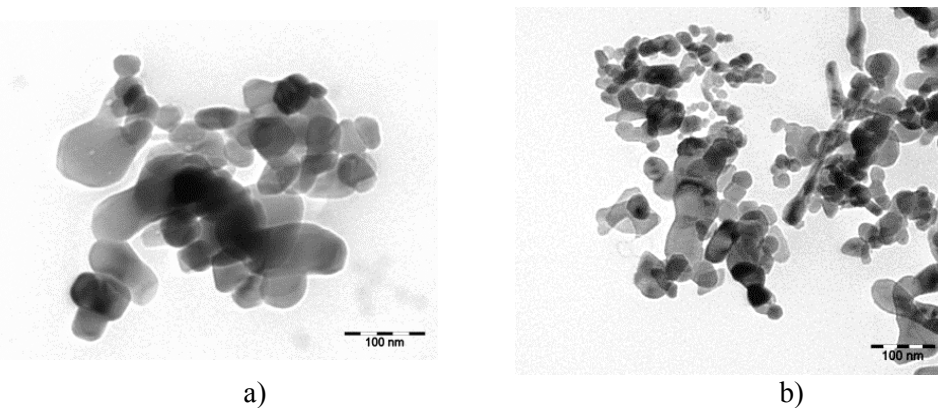
### 3.1. Dispersion of the dry particles

The results of BET and TEM analysis well correlate: the discrepancy in average particle size is no more than 15 nm (table 1).

Although particles are agglomerated (figure 1), they are connected with not phase, but interparticle interaction (coagulation). Therefore, we presume the possibility to disperse particles in aqueous suspensions, and, consequently, to adsorb surfactants on the enlarged particles surface area.

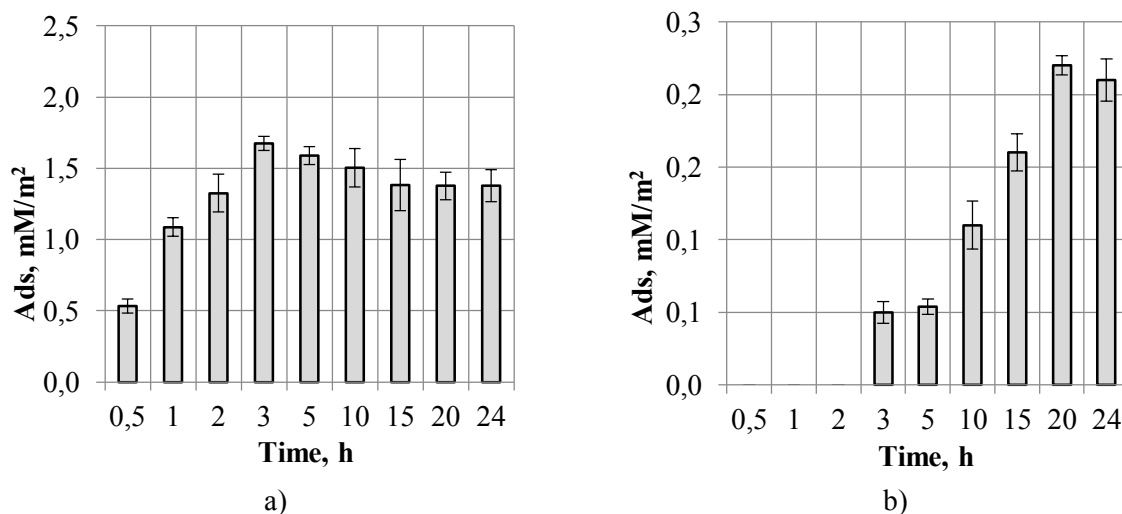
**Table 1.** Dispersion of dry particles.

Sample designation	BET data		TEM data	
	Specific surface area, m <sup>2</sup> /g	Average diameter of particles, nm	Average size of particles, nm	Average size of aggregates, $\mu$ m
TiO <sub>2</sub>	22.4 $\pm$ 0.06	66	44 $\pm$ 5	2.5 $\pm$ 0.3
ZnO	26.8 $\pm$ 0.15	40	51 $\pm$ 5	4.8 $\pm$ 5.9

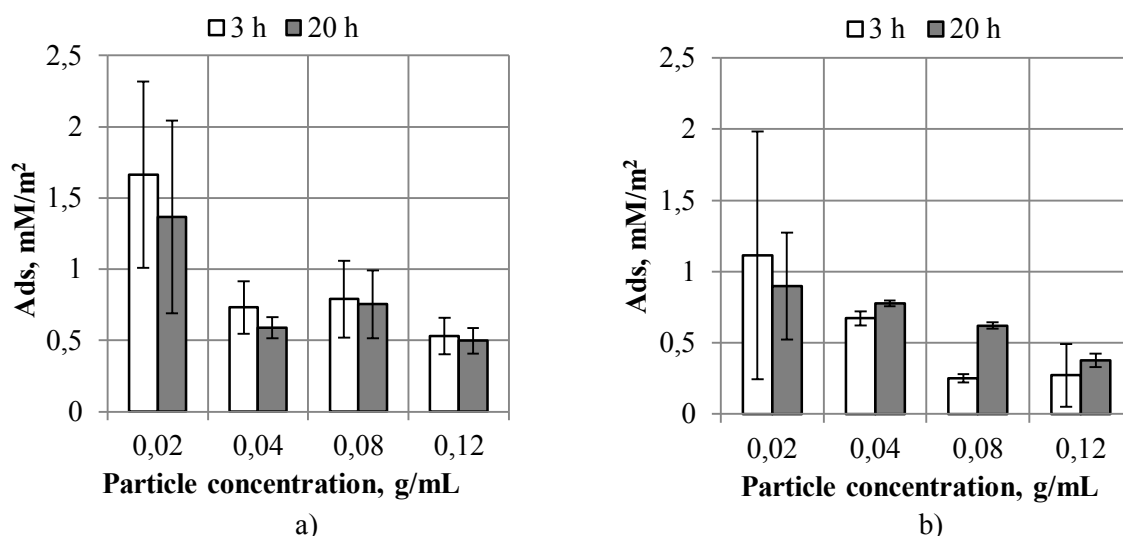
**Figure 1.** TEM images of TiO<sub>2</sub> (a) and ZnO (b) nanoparticles.

### 3.2. Effect of exposure duration on adsorption

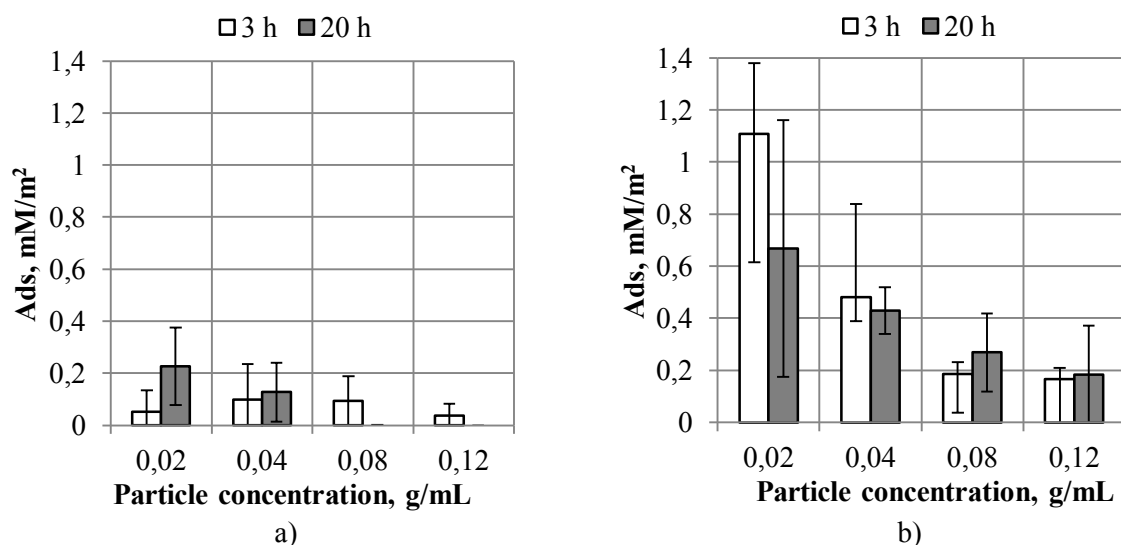
As we have shown, in Gly-suspension with particle concentration of 0.02 g/mL, surfactant at most is adsorbed during 3 h on ZnO (figure 2a, 1.68 mM/m<sup>2</sup>) and during 20 h on TiO<sub>2</sub> (figure 2b, 0.22 mM/m<sup>2</sup>) surface. Further exposure results in Ads decrease by 22 and 5% on ZnO and TiO<sub>2</sub>, respectively. The similar trend describes Glut-containing solutions: Ads value goes down by 7 and 40%, respectively, on ZnO (figure 3b) and TiO<sub>2</sub> (figure 4b) during 20 h exposure. Despite measurement error of 15%, the decrease of Ads may be explained by the surfactant desorption or aggregation of particles. However, longer exposure does not affect Ads value, and the systems tend to an equilibrium state since the surfactant concentration does not change in solution.

**Figure 2.** Time-related change of adsorption coefficient (Ads) of glycine in ZnO (a) and TiO<sub>2</sub> (b) suspension (particle concentration 0.02 g/mL, measurement deviation from triplicate results).

It has been demonstrated that in more concentrated suspensions (0.08...0.12 g/mL) the adsorption coefficient varies differently during a day-exposure: the change depends on surfactant and NPs compositions. For instance, in 0.08 g/mL suspensions of ZnO NPs Ads decreases by 4% in Gly (figure 3a) compared to 20% in Glut (figure 3b). In TiO<sub>2</sub> suspensions there is no adsorption of Gly after 20 h exposure (total desorption, figure 4a), although in Glut solution Ads rises by 44% (figure 4b). Since we have different time-related influence on Ads, the effect of particles concentration on nanoparticles properties has been determined both at 3 and 20 h exposure. We see that exposure of TiO<sub>2</sub> with particle concentration of 0.02 g/mL during 20 h leads to four times gain of Ads<sub>Gly</sub>. Nevertheless, growth of NPs content up to 0.08 g/mL results in desorption of Gly molecules from TiO<sub>2</sub> particles after 20 h aging (figure 4a).



**Figure 3.** Concentration-related change of adsorption coefficient (Ads) of glycine (a) and L-glutamic (b) for ZnO NPs (measurement deviation from triplicate results).



**Figure 4.** Concentration-related change of adsorption coefficient (Ads) of glycine (a) and L-glutamic (b) for TiO<sub>2</sub> NPs (measurement deviation from triplicate results).

### 3.3. Effect of nanoparticles concentration on adsorption

According to experimental data, suspensions dilution promotes amino acids adsorption on NPs, although the concentration effect decays in suspension with higher particles content. For example, after the dilution of 3 h aged suspension from 0.04 till 0.02 g/mL there is a two-time drop of Ads value on the average (by 2.3 and 1.6 times on ZnO NPs in Gly and Glut, respectively, figures 3a and 3b, and by 2.4 times on TiO<sub>2</sub> NPs in Glut, figures 4a and 4b).

In higher concentrated suspensions (0.08...0.12 g/mL) the Ads shift is insignificant and the value changes within the measurement error. Generally, six-fold decrease of concentration (from 0.12 to 0.02 g/mL) leads to the growth of the Ads by 3.1...4.1 times (figure 3a and 3b) on ZnO and by 6 times (figure 4b) on TiO<sub>2</sub> NPs. Thus, to obtained results, regardless surfactant nature and exposure time, higher content of particles brings to lower adsorption coefficient calculated per specific surface of particles. Actually, if to measure the amount of surfactant adsorbed on NPs and relate it to maximum amount of surfactant which may adsorb onto NPs, we see that this value considerably increases with growth of NPs content. For example, in TiO<sub>2</sub> suspensions with ratio 'NPs:Glut' 1:15..1:8..1:4..1:2.5 adsorption portion is 0.30..0.36..0.27..0.44. However, while in concentrated suspensions the surface of particles is larger (0.52 m<sup>2</sup> in 1 mL of 0.02 g/mL compared to 3.12 m<sup>2</sup> for 0.02 g/mL), the activity of surface tend to decrease. It was also demonstrated by comparing IR spectra obtained on TiO<sub>2</sub> NPs (10<sup>-4</sup> M) exposed to differently concentrated Glut-solutions (10<sup>-6</sup>...10<sup>-3</sup> M at pH=3 during 40 min) [25]. The authors revealed double growth of adsorption peak height at 1408 cm<sup>-1</sup> at 10-fold increase of weight ratio 'NPs:Glu' (from 50:1 to 5:1), while we obtained 4-times decrease of IR peak height of the solution separated from NPs for the ratio 'NPs:Glu'=1:2.5 compared 1:15 to.

### 3.4. Effect of surfactant ionogenicity on adsorption

We have compared nonionic surfactant (Gly) and an ionic one (Glut) giving negatively charged particles in solution. In the experiments, we remained the pH of solutions obtained after surfactant dissolution, namely, 6.5 for Gly and 9.5 for Glut, since the adsorption is higher for Gly in acidified medium and Glut in alkali medium [25]. It has been shown that in all ZnO suspensions regardless exposure time there is 1.5 times difference in Ads in favor of nonionic surfactant (0.02...0.04 mg/L), and this effect becomes stronger in 0.08..0.12 mg/L suspensions, where Gly adsorption is 3 times more effective compared to Glut (figure 3). Thus, under certain conditions both glycine and L-glutamic are better adsorbed on ZnO NPs, while the adsorption of glycine on the surface more efficient that was theoretically confirmed by simulation studies [30-31].

However, in diluted TiO<sub>2</sub>-based suspensions there is reverse tendency: adsorption of ionic surfactant is much higher than nonionic one and this effect goes down at NPs content growth. Thus, for 3 h aged suspension with concentration of 0.02...0.04...0.08 g/mL the value of Ads<sub>Glut</sub> / Ads<sub>Gly</sub> is 22...4...2, respectively. Higher adsorption of Glut is in agreement with theoretical simulations of amino acids adsorption at the rutile surface in aqueous solution, where the authors have found that the probability of interaction between the adsorbate and the surface is 3.7 times higher for Glut compared to Gly [16, 18], and confirmed by experimental amino acid adsorption results [17, 25].

## 4. Conclusion

We have shown the influence of the exposure duration on adsorption properties of industrial ZnO and TiO<sub>2</sub> nanoparticles with an average size of 40-60 nm in a particle concentration range of 0.02...0.12 g/mL exposed to 2M aqueous solutions of aminoacetic and glutamic acids. It has been revealed that in concentrated suspensions (0.08...0.12 g/mL) Ads value does not change significantly in time, whereas in diluted NPs suspensions (0.02...0.04 g/mL), exposure time and surfactant nature is highly critical for adsorption coefficient. Day exposure of NPs may result in slight desorption as shown on ZnO NPs or total desorption of surfactant as shown on TiO<sub>2</sub> NPs in Gly solutions. Generally, six times dilution (from 0.12 to 0.02 g/mL) of NPs suspensions may lead to Ads augmentation by 3...6 times. When comparing surfactants it has been demonstrated that regardless

exposure time and particle concentration nonionic surfactant (glycine) is adsorbed in 1.5...3 times better on ZnO, although in diluted TiO<sub>2</sub> suspensions there is reverse tendency.

From a methodological view point, a comparative study of NPs adsorption properties in amino acid solutions is substantiated by infrared spectroscopy at 1300...1400 cm<sup>-1</sup>. Based on the obtained results it has been concluded that in order to provide effective comparative study of NPs adsorption properties it is not reasonable to concentrate the NPs suspension more than 0.04 mg/L and it is better to expose them during 3 h in order to avoid surfactant desorption.

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