

## The properties of silica nanoparticles modified with cationic surfactant

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The properties of SiO<sub>2</sub> nanoparticles interface modified with cationic surfactant molecules has been studied. Using a fluorescent indicator 2,7-dichlorofluorescein as the surface probe, it has been demonstrated that a bilayer is formed on the SiO<sub>2</sub> surface providing similarity of the nanoparticle surface in aqueous media with that of surfactant micelles.

Проведено исследование свойств наночастиц SiO<sub>2</sub>, модифицированных молекулами катионного поверхностно-активного вещества (ПАВ). С использованием флуоресцентного индикатора 2,7-дихлорфлуоресцеина в качестве поверхностной пробы показано, что на поверхности SiO<sub>2</sub> образуется бислой, придающий поверхности наночастиц в водной среде сходство с поверхностью мицелл ПАВ.

Silica nanoparticles are of great interest in the field of nanotechnology and nanotechnology development [1, 2]. The silica nanoparticles modified with cationic surfactant molecules are widely used for creating a number of functional materials [1-5]. For example, the sol-gel matrixes obtained on the basis of tetraethoxysilane and surfactant, show numerous favorable properties [3, 4]; furthermore, the use of silica modified with surfactant provides the synthesis of biomarkers [5]. However, many properties of the silica nanoparticles surface coated with surfactant molecules have not yet been clarified. The interaction between cationic surfactants and silica surface is well manifested [6-10], but the character of structures formed by surfactant on the SiO<sub>2</sub>/water interface is still in question. That is why the purpose of the present work

was to investigate the silica nanoparticles coated with surfactant adlayer (presumably bilayer) and to find out whether these modified species resemble the surfactant micelles in affecting the state of fluorescent dye 2,7-dichlorofluorescein. The latter was already used before as a probe for cationic micelles. Such modified nanoparticles can be used for creation of sensor devices.

We have studied the surface of 85 nm diameter SiO<sub>2</sub> nanoparticles (in dried state), coated with cetyl trimethylammonium ions, as a medium for protolytic reactions with 2,7-dichlorofluorescein used as testing reagent. In the experiments, a special attention was paid to the choice of system composition, for a coagulation of colloidal sol and the formation of common surfactant micelles in bulk phase is possible. The silica surface state is known to depend on pH of

solution [6]. Since its zero-charge point is at pH  $\sim$ 2, the surfactant adlayer may be altered, and this fact was taken into consideration in the experimental data processing. One should also keep in mind the change in dissociation of silica surface silanol groups when a surfactant is present in the system under study.

Cetyl trimethylammonium bromide (CTAB, Sigma-Aldrich, 99 % purity) was used as commercially obtained. Sodium chloride, aqueous hydrochloric, phosphoric, and acetic acids were of analytical purity grade. 2,7-Dichlorofluorescein was used as commercially obtained. Absolute ethanol was prepared using a standard procedure. Aqueous NaOH stock solution was kept protected from carbon dioxide. Tetraethoxysilane (TEOS, Surel, 99 % purity), and ammonia solution for colloidal synthesis were used without additional purification.

The UV/VIS absorption spectra were measured using SP-46 and Hitachi U-3210 spectrophotometers. Fluorescence was measured with a Hitachi F-4010 fluorescence spectrophotometer. The pH values were measured at  $25.0 \pm 0.1^\circ\text{C}$  with the standard deviation of  $\pm(0.01-0.02)$  using a P 37-1 potentiometer and a pH-121 pH-meter equipped with an ESL-63-07 glass electrode and an Ag/AgCl reference electrode in a cell with liquid junction (1 M KCl). The cell was calibrated using standard buffers (pH = 1.68, 4.01, 6.86, and 9.18). Electron microscopy images of  $\text{SiO}_2$  sols (pure and with surfactant) were obtained using an EM-125 microscope at 100 kV accelerating voltage. The average particle size, size distribution, and  $\zeta$ -potential of  $\text{SiO}_2$  sols were determined by Dynamic and Electrophoretic Light Scattering (DLS, ELS) methods using a "Zeta Sizer Nano ZS", Malvern instrument (4 mW He-Ne-laser, 633 nm, optical filter at 633 and 532 nm). All measurements were carried out at  $25^\circ\text{C}$  under the  $173^\circ$  angle. For all our samples, the folded capillary cells (Malvern Instr.) were used in the electrophoretic mobility study and glass cuvettes to measure the size. The scattering data were analyzed by "CONTIN" algorithm. The hydrodynamic diameter was calculated from the measured translational diffusion coefficient using the Stokes-Einstein relationship. The  $\zeta$ -potential for aqueous suspension was calculated from electrophoretic mobility according to the Smoluchowski model. The applied voltage was set manually within the range of 30 to 100 V using the "DTS 4.0"

software. In every system, the  $\zeta$ -potential value was an average of 7 independent measurements with 20 runs at each voltage magnitude. Prior to electrophoretic measurements, the system was calibrated using the standard polystyrene latex DTS1050 (Malvern Instruments Ltd, UK) which has the  $\zeta$ -potential value of  $-(50 \pm 5)$  mV. The  $\zeta$ -potential error was approximately 5 to 7 %, depending on the surfactant concentration in the system.

The stock solution of 2,7-dichlorofluorescein was prepared using water as solvent, with addition of small amounts of NaOH. The stock  $\text{SiO}_2$  sol was diluted so that the working concentration was 0.28 g  $\text{SiO}_2$  per  $\text{dm}^3$ . Suitable pH values of the working solutions used for VIS-spectroscopic  $pK_a^a$  determinations were provided using acetate and phosphate buffers as well as solutions of hydrochloric acid or sodium hydroxide. The ionic strength,  $I$ , of solutions was maintained constant by adding NaCl solution. All the solutions were prepared and measurements were made at  $25^\circ\text{C}$ . The absorption and fluorescence spectra were measured in cells with the absorbing layer length of 5 cm in the case of absorption spectra and 1 cm for fluorescence measurements. The dye concentration in working solutions was within the range from  $1.7 \cdot 10^{-6}$  to  $5.7 \cdot 10^{-6}$  M.

The stock sol of colloidal silica was obtained by TEOS hydrolysis in absolute ethanol, with ammonia as catalyst, according to procedure described in literature [11], where the influence of reaction mixture composition on the particle diameter was discussed.

As mentioned above, the present work is aimed at investigation of the silica nanoparticles coated with surfactant molecules, that is why it was important to commence with the study of optical properties both of stock sol and of system containing surfactant. The system composition was chosen to be 0.28 g  $\text{SiO}_2$  per  $\text{dm}^3$  and  $3 \cdot 10^{-4}$  M CTAB (1.07 mM CTAB per 1 g  $\text{SiO}_2$ ) basing on the reasons to be discussed below. The ethanol concentration in working solutions was negligible (about 0.01 vol. %). In order to determine the average particle size, the electron microscopy and DLS method were used.

As shown by electron microscopy images,  $\text{SiO}_2$  nanoparticles in the stock sol are highly uniform with average diameter of  $85 \pm 5$  nm (Fig. 1). One should take into con-

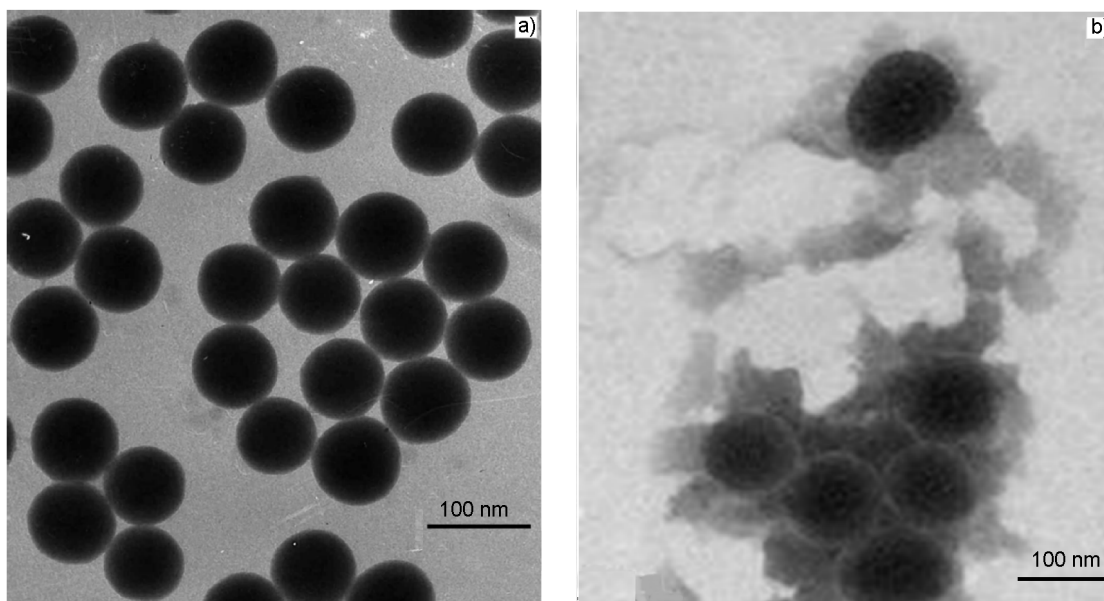


Fig. 1. Electron microscopy images of a) pure sol nanoparticles and b) CTAB-modified nanoparticles.

sideration that electron microscopy images were obtained for dried samples.

Moreover, the system shows no signs of coagulation when certain amount of surfactant is added.

The DLS experiments demonstrate that  $\text{SiO}_2$  nanoparticles in solution have the average diameter of 74 nm. In turn, the nanosized particles, presumably coated with surfactant, have average diameter of 100–110 nm (Fig. 2). One should mention that not only CTAB addition results in such increase of particle diameter. This effect is brought by enhanced hydration of the surfactant coated silica nanoparticles (hydro-sphere formation).

An essential difficulty in studying the adlayer formation is due to possible coexistence of common surfactant micelles and modified silica nanoparticles in bulk water. There are several reasons allowing us to neglect this possible effect. First, the CTAB concentration in working solutions is lower than CMC (critical micelle concentration,  $\sim 10^{-3}$  M in electrolyte-free surfactant solution), despite the fact that it may be decreased in the presence of salt. Furthermore, DLS data show that no other surfactant aggregates existed in solution except for surfactant-coated silica nanoparticles. Finally, according to literature data [6], the adsorption process dominates in such systems; consequently, all CTAB molecules are spent for bilayer formation and the presence of free micelles is hardly expected.

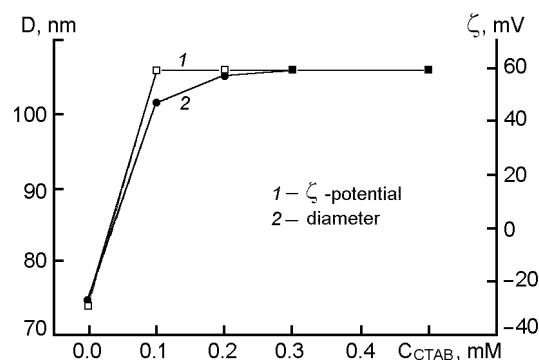


Fig. 2. The  $\zeta$ -potential (1) and particle diameter (2) of silica vs CTAB concentration.

One of the most important problems in our research was to estimate and standardize the concentration of  $\text{SiO}_2$  nanoparticles in the system. According to literature data [11], the reaction of tetraethoxysilane hydrolysis occurs with 100 % yield, so the numerical concentration of  $\text{SiO}_2$  particles in the stock sol is known. In our study, it was ca.  $1.0 \cdot 10^{17} \text{ dm}^{-3}$ . These nanosized particles are spherical and their average volume and mass concentration may be easily calculated ( $32.1 \cdot 10^{-20} \text{ dm}^3$  and  $67.5 \text{ g per dm}^3$ , respectively).

The values of  $\zeta$ -potential reflect the  $\text{SiO}_2$  surface condition both in pure sol and in system containing a certain amount of CTAB. As shown by  $\zeta$ -potential distribution data, for pure sol its value has the order of  $-27 \pm 5$  mV. Addition of CTAB concentration

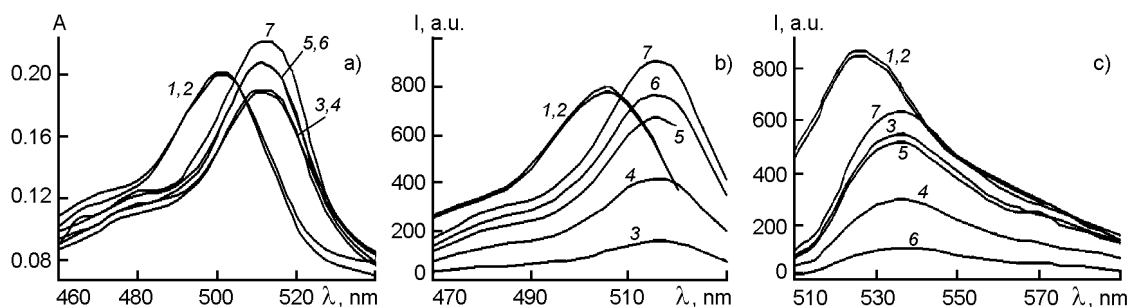


Fig. 3. a) Absorption, b) excitation and c) fluorescence spectra of 2,7-dichlorofluorescein dianion ( $\text{pH} = 10.5$ ,  $I = 0.03 \text{ M}$ ,  $c_{\text{dye}} = 1.702 \cdot 10^{-6} \text{ M}$ ): in water (1), in the presence of nanoparticles (2), in the system containing  $0.36 \text{ mM}$  CTAB per  $1 \text{ g SiO}_2$  (3), in  $1 \cdot 10^{-4} \text{ M}$  CTAB solution (4), in the system containing  $1.07 \text{ mM}$  CTAB per  $1 \text{ g SiO}_2$  (5), in  $3 \cdot 10^{-4} \text{ M}$  CTAB solution (6), in CTAB micellar solution (7).

from  $0.1 \text{ mM}$  up to  $0.5 \text{ mM}$  results in surface re-charging, and  $\zeta$ -potential increases up to  $+47 \pm 5 \text{ mV}$  (Fig. 2). These results are consistent with previous studies of silica particles in systems containing cationic surfactant [7]. The interaction of silica surface with CTAB molecules is described as follows. The surfactant monolayer formation is defined by electrostatic interaction between the positively charged surfactant headgroups and surface silanol groups. The driving force of the second layer formation is hydrophobic interaction between surfactant tails. There are several models describing this process including reverse orientation model, bilayer, and small micelle models [7, 9].

Over and above, silica colloidal sols are known to coagulate when CTAB amount is insufficient to form species lyophilized enough [7]. To find an optimal system composition, i.e. conditions where this phenomenon is not observed, we performed series of corresponding experiments. When  $\text{SiO}_2$  concentration is near to  $0.28 \text{ g per dm}^3$  and surfactant concentration near to  $5 \cdot 10^{-6} \text{ M}$ , no visible changes occur. An increase in CTAB concentration up to  $5 \cdot 10^{-5} \text{ M}$  results in rapid coagulation of sol due to both neutralization and hydrophobization of the charged surface. Further addition of cationic surfactant (up to  $3 \cdot 10^{-4} \text{ M}$ ) stabilizes the system. This fact is likely to be, as first approximation, the result of bilayer formation according to well-described dispersion-coagulation-re-dispersion sequence [7–10]. With CTAB present in solution, such system remains stable when an electrolyte (NaCl) is added until ionic strength is less than  $0.04\text{--}0.05 \text{ M}$ . Note that the degree of CTAB dissociation in micelles is quite low and a considerable part

of counterions remains in Stern layer. Taking into account the surface area of nanoparticles and area occupied by one CTAB headgroup ( $0.474 \text{ nm}^2$ ) [12], we have estimated the  $\text{SiO}_2/\text{CTAB}$  ratio necessary for bilayer formation. It is as follows:  $0.28 \text{ g SiO}_2 \text{ per dm}^3$  and  $3 \cdot 10^{-4} \text{ M}$  CTAB or  $1.07 \text{ mM}$  CTAB per  $1 \text{ g SiO}_2$ . Our results are in good agreement with those obtained by Wang et al. [7], who reported that bilayer had been formed when the CTAB concentration was  $\approx 1 \text{ mM}$  per  $\text{g SiO}_2$  (with average particle diameter in dried state  $100\text{--}110 \text{ nm}$ ). The porosity and fractal structure of such colloidal species should also be noted [7], since the calculated CTAB amount may not be sufficient for bilayer formation. The  $\text{pK}_a$  value of surface silanol groups ( $\text{SiOH}$ ) can be affected by surfactant, and this fact has been taken into consideration either.

The spectral properties of fluorescein and its derivatives are very sensitive to microenvironment nature [13–15]. Thus, comparing the absorption, fluorescence and excitation spectra of the dianion in systems containing silica and CTAB as well as in surfactant solutions provides the information on morphology of surfactant bilayer. The key question of our research is whether these modified silica nanoparticles resemble the common surfactant micelles in the view of affecting the acid-base equilibrium of the dye, attached to surfactant-coated silica.

Absorption, fluorescence and excitation spectra of 2,7-dichlorofluorescein dianion (I) (Chart 1) are presented in Figure 3.

There are certain differences between the systems containing modified silica nanoparticles and surfactant solutions, especially in fluorescence and excitation spectra. Thus,

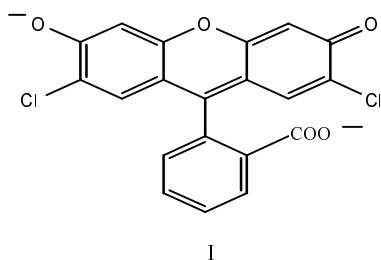
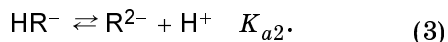
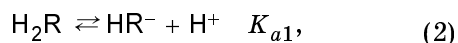
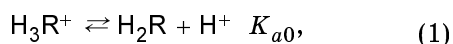


Chart 1. 2,7 - Dichlorofluorescein dianion

excitation spectra of 2,7-dichlorofluorescein in solutions containing  $1 \cdot 10^{-4}$  M CTAB have low intensities as compared to the system under investigation and CTAB micelles. The same effect has been observed for fluorescence spectra. In all cases, the differences between spectral properties of the dye in water and in solution, containing  $\text{SiO}_2$ , were inconsiderable. Evidently, the interfacial adlayer is formed in the system containing 0.28 g  $\text{SiO}_2$  per  $\text{dm}^3$  and  $3 \cdot 10^{-4}$  M CTAB (1.07 mM CTAB per 1 g  $\text{SiO}_2$ ), but the surfactant-coated silica nanoparticle does not behave particularly like surfactant micelle. When CTAB concentration is reduced, the surfactant adlayer does not seem to be completed and formation of dye/surfactant aggregates adsorbed onto the silica surface takes place.

The silica nanoparticles coated with surfactant adlayer were expected to affect the dye state in a manner like that of common surfactant micelles. In order to confirm this supposition, we examined the acid-base equilibrium of 2,7-dichlorofluorescein in the system containing 0.28 g  $\text{SiO}_2$  per  $\text{dm}^3$  and  $3 \cdot 10^{-4}$  M CTAB.

The ionization of 2,7-dichlorofluorescein in solutions proceeds in three steps [13]:



The first equilibrium cannot be studied here since the value of  $pK_{a0}$  is rather low (ca. 0.2), and solutions with extremely low pH are required. Silica surface is known to be re-charged at pH lower than 2, which may bring about the alteration or even degradation of surfactant bilayer, although the zero charge point may be reduced due to the presence of CTAB.

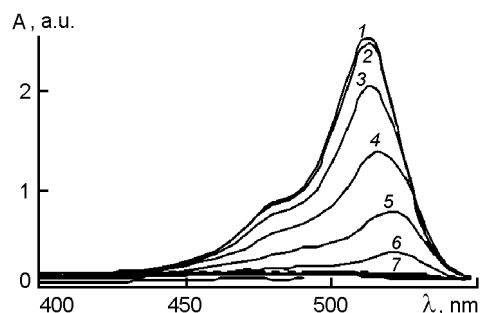


Fig. 4. Adsorption spectra of 2,7-dichlorofluorescein in the presence of silica and surfactant at different pH ( $I = 0.03$  M,  $c_{\text{dye}} = 5.68 \cdot 10^{-6}$  M): 10 (1), 5.35 (2), 4.35 (3), 3.68 (4), 2.72 (5), 1.91 (6), 1.54–1.01 (7; here  $I \geq 0.03$  M).

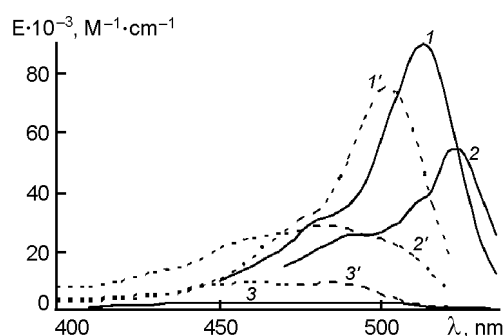
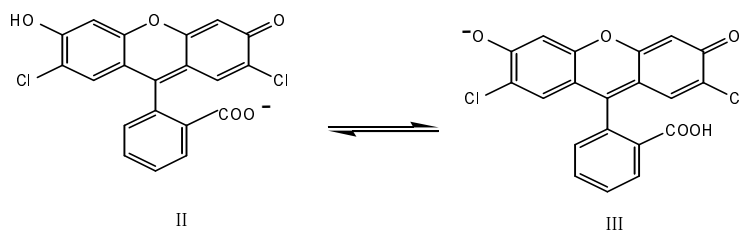


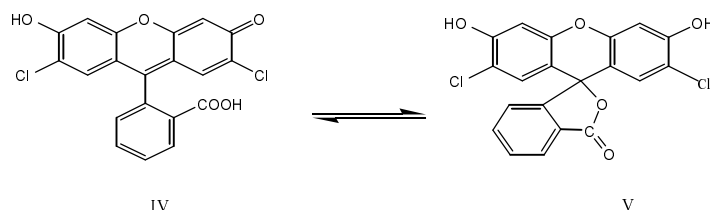
Fig. 5. Absorption spectra of various indicator forms in the system containing 0.28 g  $\text{SiO}_2$  per  $\text{dm}^3$  and  $3 \cdot 10^{-4}$  M CTAB and in water (dotted line): 1,1' —  $\text{R}^{2-}$ ; 2,2' —  $\text{HR}^-$ ; 3,3' —  $\text{H}_2\text{R}$ .

We have determined the apparent  $pK_{a1}^a$  and  $pK_{a2}^a$  values basing on absorbance (A) vs. pH dependence according to method described elsewhere [13]. In working solutions, pH was ranged from 1.12 to 12.00 (16 solutions altogether). The wavelength range was 400–550 nm. Calculations were performed using CLINP software created by Yu.V.Kholin [16]. The absorption spectra of the fluorophor in the investigated system at different pH are typified in Fig. 4.

We have obtained the following results. The  $pK_{a1}^a$  and  $pK_{a2}^a$  values in the investigated system are  $3.26 \pm 0.01$  and  $4.05 \pm 0.02$ , respectively. Those are markedly lower than in water: ( $4.00 \pm 0.10$  and  $5.19 \pm 0.06$ , respectively). The behavior of 2,7-dichlorofluorescein has been investigated before in micelles of cetyl pyridinium chloride (0.05 M KCl), and the following values of  $pK_{a1}^a$  have been obtained:  $3.58 \pm 0.08$  and  $3.70 \pm 0.12$



Scheme 1.



Scheme 2.

[15]. Thus, the acid-base equilibrium of the dye is considerably shifted as compared with water, and this effect is almost similar to that in surfactant micelles. This phenomenon can be explained on the basis of the following well-known equation, which shows the relation between the surface electrical potential and the apparent ionization constant values [15]:

$$pK_a^a = pK_a^w + \log \frac{\gamma_B}{\gamma_{BH}} - \frac{\Psi F}{2.3RT}, \quad (4)$$

where  $pK_a^w$  is thermodynamical ionization constant in water;  $\Psi$  is electrical potential in the localization region of the indicator;  $\gamma$  are activity coefficients of transfer from water to the pseudophase;  $F$  is the Faraday constant;  $R$  is gas constant. Since the surface of the surfactant-coated silica nanoparticle is positively charged, the lowering of  $pK_a^a$  values in comparison with water is of the same nature as in cationic surfactant micelles. The absorption spectra of various indicator forms are presented in Fig. 5. The  $R^{2-}$  and  $H_2R$  spectra are obtained directly at  $pH = 11.00$  and  $1.12$ , respectively. The  $HR^-$  spectrum was singled out of the spectra of equilibrium mixtures ( $H_2R \rightleftharpoons HR^- \rightleftharpoons R^{2-}$ ), having the  $pK_a^a$  values, following the procedure described before [13]. The shifts for absorption spectra are typical of organic solvents or micellar systems:  $\lambda_{max}$  values for  $R^{2-}$ ,  $HR^-$ ,  $H_2R$  in the presence of modified silica nanoparticles are 510, 505 and 520, 470 and 500 nm, respectively, while in water, 500 ( $R^{2-}$ ), 485 ( $HR^-$ ), 460 and 485 nm ( $H_2R$ ).

The  $R^{2-}$  maximum shift is of solvatochromic nature, while the other effects are caused by tautomeric transformations of  $HR^-$  and  $H_2R$ .

Fig. 5 demonstrates that the absorption maximum of 2,7-dichlorofluorescein monoanion is shifted toward the red as compared to that of dianion. Such effect is always observed when passing from aqueous solutions to organic media as well as in micellar solutions [15]. Consequently, the tautomeric equilibrium of  $HR^-$  is in turn shifted from (II) to (III) according to Scheme 1.

Decoloration of solutions, where  $H_2R$  form of the dye dominates when passing from water to the colloidal system under study is caused by the tautomeric equilibrium shift from the colored quinone (IV) to the colorless lactone (V) (Scheme 2).

Hence, the observed spectra and obtained values of  $pK_a^a$  reflect the specific properties of surfactant-coated silica surface and the way it affects acid-base and tautomeric equilibrium of the luminophore. The described behavior of various indicator forms in the system containing silica and surfactant is similar to that in the surfactant micelles [15], which indicates the formation of surfactant bilayer on the silica surface.

Thus, the interfacial properties of surfactant-coated silica nanoparticles were studied by using luminescent dye 2,7-dichlorofluorescein as a test substance. Basing on the absorption, excitation, and fluorescence spectra analysis, the bilayer of cetyl trimethylammonium bromide molecules has been found to be formed when the system composition is 1.07 mM CTAB per 1 g  $SiO_2$  (0.28 g  $SiO_2$  per  $dm^3$  and  $3 \cdot 10^{-4}$  M CTAB). The fluorophore acid-base equilibrium was examined in this system and apparent acid-

base equilibrium constants were calculated. The latter ones have turned to be lower than in water, which is typical of micellar systems and may be an evidence of surfactant bilayer formation on the surface of silica nanoparticles. It was found that absorption spectra of conjugated dye forms were shifted as compared to water, which is caused by solvatochromic effect for dianion and tautomeric transformations of  $\text{HR}^-$  and  $\text{H}_2\text{R}$  forms. This effect resembles in general features the dye behavior in cationic surfactant micelles, but there are differences in the excitation and fluorescence spectra which are caused by the specificity of surface adlayer morphology and character of dye binding.

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## Властивості наночастинок кремнезему, модифікованих катіонною поверхнево-активною речовиною

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Проведено дослідження властивостей наночастинок  $\text{SiO}_2$  що модифіковані молекулами катіонної поверхнево-активної речовини (ПАР). З використанням флуоресцентного індикатора 2,7-дихлорфлуоресцеїну як поверхневої проби показано, що на поверхні  $\text{SiO}_2$  утворюється бішар, що надає поверхні наночастинок у водному середовищі подібність із поверхнею міцел ПАР.