

Influence of Ionic Surfactants and Lecithin on Stability of Titanium Dioxide in Aqueous Electrolyte Solution*

Emil Chibowski,** Lucyna Holysz, Konrad Terpilowski, and Agnieszka Ewa Wiacek

*Department of Physical Chemistry-Interfacial Phenomena, Faculty of Chemistry,
Maria Curie-Skłodowska University, 20-031 Lublin, Poland*

RECEIVED NOVEMBER 17, 2006; REVISED MAY 25, 2007; ACCEPTED JUNE 4, 2007

Keywords
titanium dioxide
suspension stability
zeta potential
effective diameter
sedimentation rate
surfactants
lecithin

Zeta potential, effective diameter and sedimentation rate of TiO₂ (Degussa P-25) suspension were studied in the presence of NaCl and anionic (sodium dodecyl sulfate, SDS) or cationic (dodecyltrimethylammonium bromide, DTAB; tetradecyltrimethylammonium bromide, TTAB; and hexadecyltrimethylammonium bromide, CTAB) surfactant, as well as lecithin (1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine, DPPC). In the experiments, the concentration of surfactants (lecithin) and pH of the solutions were varied. The results obtained show significant influence of the surfactants on the measured quantities. Depending on the concentration of the surfactants and pH, they stabilize or destabilize the suspension. The anionic SDS surfactant is more effective than the cationic ones used in the process of suspension stabilization/destabilization. At the concentrations used, lecithin (DPPC) affects the parameters only at natural (not regulated) pH of the suspension. At 5 mg dm⁻³ it stabilizes TiO₂ suspension while at 10 mg dm⁻³ some destabilizing effects appear relative to the DPPC-free suspension.

INTRODUCTION

Investigations of physicochemical and electrochemical properties of titanium dioxide in water and/or electrolyte solutions have been studied for many years. Titania is often used as a model oxide in the studies of electrical double layers properties. Among other things, this is because of the position of the point of zero charge close to the middle of the pH scale.^{1–8} It allows studying changes in its positive and negative surface charge in a wide range of pH and ionic strengths.⁹ On the other hand, titanium dioxide has numerous practical applications, *e.g.*, as a pigment, filler in many polymers, catalyst and photocatalyst, ceramic membranes and an inorganic UV

filter.^{10–15} Titanium dioxide is believed to be a non-toxic solid and it is therefore used in cosmetic products, in some pharmaceuticals and foodstuffs.^{16,17}

Most dispersed systems show low stability, even if the degree of their dispersion is high. Solid particles in a suspension show a tendency to aggregate and then sediment. Stability of aqueous dispersions depends upon the balance of interactions between the particles of the dispersed phase, which are of attractive London dispersion forces and repulsive electrostatic interactions between the electrical double layers at the solid/solution interface, as well as the interactions caused by the presence of the adsorbed layers (steric stabilization) and hydration forces.

* Dedicated to Professor Nikola Kallay on the occasion of his 65th birthday.

** Author to whom correspondence should be addressed. (E-mail: emil@hermes.umcs.lublin.pl)

Stability of such systems can be modified by changing the electrostatic interactions and the structure of adsorbed layers. To obtain stable suspensions of titanium dioxide, ionic and nonionic surfactants are added.^{5,18–23} Obviously, the stability of TiO₂ dispersions depends also on various parameters, *i.e.*, the density and size of the particles, particle size distribution, pH, type of electrolyte and ionic strength.

The aim of this paper was to compare the effect of anionic (sodium dodecyl sulfate – SDS) and three cationic surfactants of increasing alkyl chain: dodecyltrimethylammonium bromide – DTAB, tetradecyltrimethylammonium bromide – TTAB, hexadecyltrimethylammonium bromide – CTAB on the stability of titanium dioxide suspensions in the presence of 10⁻³ mol dm⁻³ NaCl solution at different pH. Natural stabilizer (lecithin), 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine – DPPC was also used for this purpose.

EXPERIMENTAL

Materials

TiO₂ (P-25, Degussa), NaCl (analytical grade reagent, Standard, Poland), NaOH and HCl (analytical grade reagent, POCH S.A., Poland), SDS (99 %, Fluka), DTAB (99 %, Sigma), TTAB (99 %, Sigma), CTAB (99 %, Sigma), DPPC (99 %, Sigma), deionized water from the Millipore Q-Plus 185 system.

Purification of TiO₂. – To remove impurities, titanium dioxide was purified by the procedure described by Preočanin and Kallay.¹ For this purpose, a 25-g sample of TiO₂ was placed in a polycarbonate glass beaker and 0.5 dm³ of deionized water was added. The suspension of TiO₂ was sonicated for 30 min and the pH was adjusted by adding small portions of 0.1 mol dm⁻³ NaOH solution to obtain pH ≈ 7, *i.e.*, close to the isoelectric point. After achieving this pH, the particles aggregated and their sedimentation occurred. The supernatant was then separated from the sediment by decantation and the resulting pH and the conductivity of supernatant were measured. In the next stage, 1 dm³ of deionized water was added to the sediment and the suspension was sonicated for 20 min and decanted again. This procedure was repeated until the supernatant conductivity reached the value of about 5 μS cm⁻¹. Then, purified powder of TiO₂ was dried at 100 °C. It was then treated in Fisher's mill for 3 h and again dried at 200 °C for 3 h. Thus prepared TiO₂ powder was stored in a desiccator.

TiO₂ Suspensions. – Suspensions of titanium dioxide were prepared by mixing 5 mg of purified TiO₂ powder in 100 cm³ of 10⁻³ mol dm⁻³ NaCl. Before the measurements, all the suspensions of TiO₂ were sonicated by means of a sonicator 3000 (Misonix) for 3 min.

TiO₂ Suspensions at Different pH. – The pH value of the suspension was regulated by adding a suitable amount of 0.1 mol dm⁻³ NaOH or HCl and was then measured using an Elmetron pH-meter, Poland. The suspension was left for 3 h and then the pH of suspension, zeta potential, effective diameter and sedimentation rate were determined. These parameters were again determined after 24 h. The influence of pH on the suspension properties was studied in the pH range from 3 to 10.7. The pH values of suspension were practically the same after 24 h because the TiO₂ content was small and the equilibrium had already been set during the first 3 h.

TiO₂ Suspensions with Surfactant. – First 250 cm³ of the suspension containing 12.5 mg TiO₂ at natural (not regulated) pH or pH of about 3 or 10.4 were prepared and left for 3 h. After that time, 5 samples of 50 cm³ volume each were pipetted and 1 cm³ of the studied surfactant solution was added. The added amounts of the surfactants corresponded to the following concentrations: SDS – 10⁻⁵, 10⁻⁴, 5 × 10⁻⁴ and 5 × 10⁻³ mol dm⁻³; DTAB – 5 × 10⁻⁴, 10⁻³, 5 × 10⁻³ and 10⁻² mol dm⁻³; TTAB and CTAB – 10⁻⁶, 10⁻⁵, 5 × 10⁻⁵ and 5 × 10⁻⁴ mol dm⁻³. In all studied systems, surfactant concentrations were below the critical micellization concentration (*c.m.c.*) in the presence of 10⁻³ mol dm⁻³ NaCl.²⁴ In the case of SDS, the properties of TiO₂/NaCl system were studied at the natural pH of the suspension and pH ≈ 3. The influence of cationic surfactant on titania suspension was determined at natural pH of the suspension and pH ≈ 10.4.

All suspensions with the surfactants and the presence of 10⁻³ mol dm⁻³ NaCl were equilibrated for 24 h at 20 °C, and during that time they were hand shaken several times. The pH of suspensions was measured after their preparation and after 24 h, and it remained practically constant throughout the experiment.

TiO₂ Suspensions with DPPC. – First, the suspensions of TiO₂ at its natural pH, pH of about 3 and 10 were prepared. After 3 h of equilibration 3 samples of 100 cm³ volume each were pipetted out and 0.5 or 1 cm³ of DPPC solution containing 1 mg of DPPC in 1 cm³ was added. After equilibration for 24 h the pH, zeta potential, effective diameter and sedimentation rate were measured for the samples with adsorbed DPPC. The same measurements were done for the reference system without DPPC.

Measurements of Zeta Potential and Effective Diameter

Both the zeta potential and the particle size of the titanium dioxide were determined with the help of a Zeta-PALS/BI-MAS apparatus (Brookhaven Co., USA) in which the dynamic light scattering technique was applied for determination of these quantities. For each suspension sample, 10 measuring runs with 7 cycles in each run were taken. All these experiments were carried out at 20

± 1 °C and repeated two or three times. The zeta potentials of TiO₂ particles were calculated from the electrophoretic mobility using the Smoluchowski equation, which was appropriate for most of the systems studied. This is because the ionic strength of the solution was 10^{-3} mol dm⁻³ and the particle size of TiO₂ ranged from 0.2 to 21 µm (aggregated), as determined by dynamic light scattering. Hence, the κa product lay between 21 and 2180 for the aggregated particles.

Measurements of the Sedimentation Rate

Sedimentation rates of the titanium dioxide particles were determined with the help of an optical analyzer TURBISCAN Lab, whose scanning head acquires transmission and backscattering light signal every 40 µm while moving along the 55 mm cell height.²⁵ This apparatus allows to track the changes in particles aggregation and sedimentation of particle dispersion from 5 nm to 1 mm and particle concentration up to 95 % *v/v* (particle volume / liquid volume). An example of the plots obtained from the apparatus protocol is shown in Figure 1. It represents the transmission light signal of TiO₂ suspension in NaCl solution. Measurements were taken for 3 h- and 24 h-old suspensions. It is clearly seen that the transmission light signal is very similar in both samples and it is almost constant along the whole length of the cell during 1 h of scanning every 5 min, except for the first scanning taken after 10 min.

RESULTS AND DISCUSSION

As mentioned in the Introduction, titanium dioxide is a model metal oxide used in studying the properties of the interfacial electrical layer.^{1–9,26–28} Point of zero charge

(p.z.c.) and isoelectric point (i.e.p.) are two major parameters characterizing this layer. If no specific adsorption of the ions present in the solution takes place on the oxide surface, and the counterions adsorption is symmetrical, then the pH at which the p.z.c. and i.e.p. occur is the same.^{1,4,6} However, the investigated oxides are often doped with some impurity ions originating from sample preparation or being build-in if, for example, a mineral sample of the oxide is used. Therefore, the literature values for both the p.z.c. and/or the i.e.p. very often differ for the same kind of oxide.⁴ Preočanin and Kallay¹ have lately elaborated a very useful procedure of sample cleaning before using it for electrochemical experiments. This procedure has been applied in this study. A thus prepared stock sample was used for the experiments.

Figure 2 presents the results on the zeta potential, effective diameter and sedimentation rate for the TiO₂ sample as a function of pH. Measurements were carried out for 3h- and 24h-old suspensions. As can be seen, the zeta potentials are practically the same irrespective of the equilibration time. At pH values far from pH_{iep}, only a small decrease both in positive and negative values takes place after 24 h compared to the 3 h-equilibrated suspension (Figure 2a). The pH_{iep} is found to be at pH = 6.25, which is in agreement with most literature data for Degussa TiO₂, which is mostly anatase.^{1,4,5} Large changes in the effective diameter that took place during 24 h are seen in Figure 2b, but only around pH_{iep}. In older suspension, the diameter increased by 100 %, *i.e.*, from *ca.* 3.2 to 6.7 µm and was extremely pH dependent. However, the sedimentation rate as a function of pH was practically the same in 3 h- and 24 h-old suspensions as determined by means of Turbiscan. Obviously, each sample was shaken before being inserted into the measuring cell of the instrument. Good concurrence of the pH_{iep},

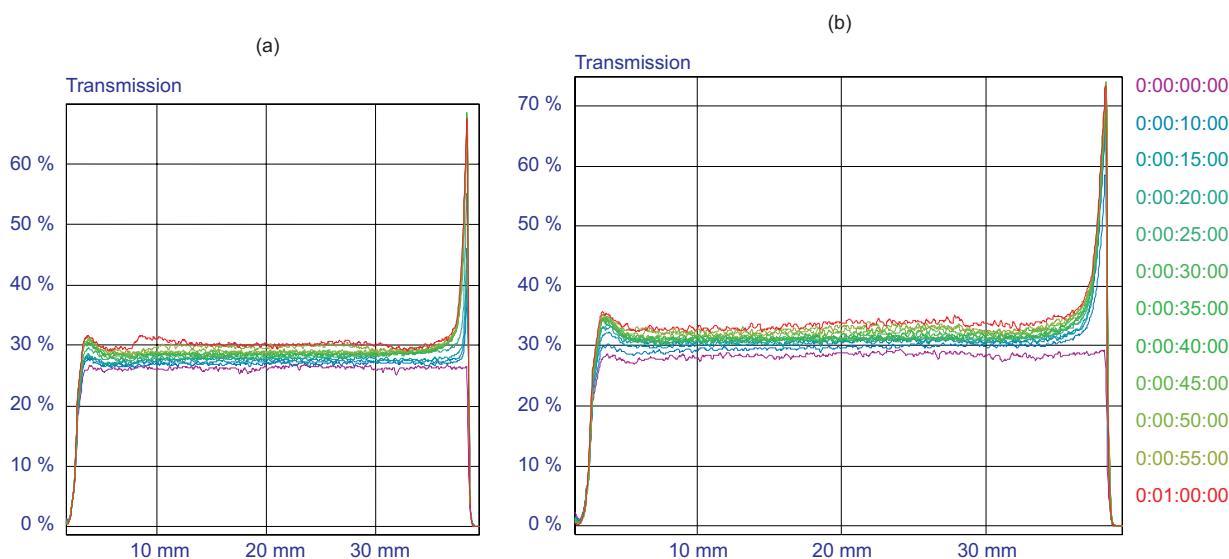


Figure 1. The transmission light signal of TiO₂ suspension in NaCl solution as a function of the height in sample cell after 3 h (a) and 24 h (b) from the moment of suspension preparation.

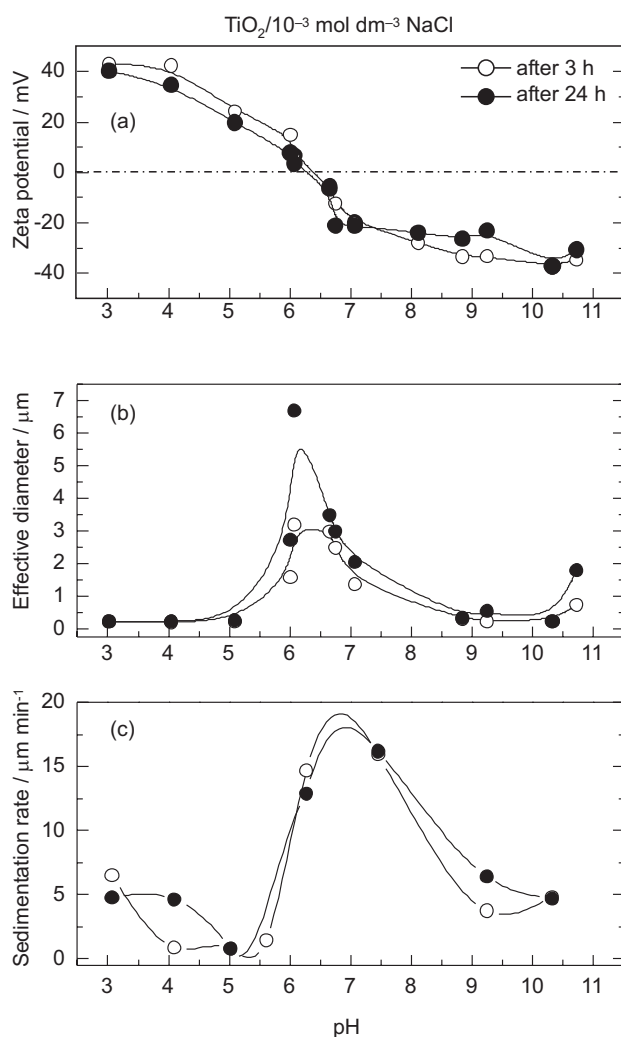


Figure 2. The zeta potential, effective diameter and sedimentation rate of TiO_2 particles in NaCl solution as a function of pH after 3 h and 24 h from suspension preparation.

maximum of the effective diameter and the sedimentation rate can be seen. It is worth mentioning that an increase in ionic strength takes place at low and high pH values. This is because the concentration of the supporting electrolyte NaCl was $10^{-3} \text{ mol dm}^{-3}$. One can also consider the effect of hydrogen bonding between water molecules and surface hydroxyl groups. However, as mentioned above, close to the pH_{iep} in the aggregation and sedimentation processes, lack of electrostatic interactions seems to play a significant role. The effective diameter *vs.* zeta potential relationship is presented in Figure 3. A marked change in the effective diameter occurs if the zeta potential changes only by *ca.* 12.5 mV (from positive 7.5 mV to negative -5 mV). This means that the pH at which the zeta potential is zero is of the greatest importance for suspension instability. The effective diameter only slightly changes if the zeta potential changes from -5 mV to -20 mV. It should be noted that this drastic change in the effective diameter takes place in a

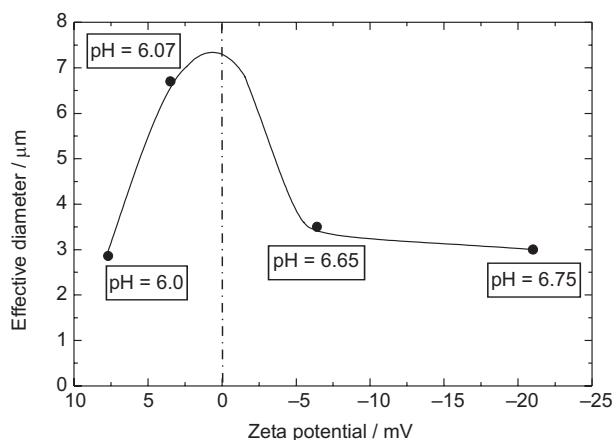


Figure 3. Effective diameter as a function of the zeta potential of TiO_2 particles in NaCl solution at pHs close to pH_{iep} .

very narrow pH range from 6.0 to 6.65 (Figure 3). The results presented in Figures 2 and 3 are important for preparation of stable TiO_2 suspensions in practical systems.

$\text{TiO}_2 / 10^{-3} \text{ mol dm}^{-3} \text{ NaCl} + \text{SDS}$ System

The influence of anionic SDS presence in the system on the zeta potential and stability of TiO_2 suspension at $\text{pH} = 3$ and natural pH (5.6–6) is presented in Figure 4. The arrows show the respective values for reference suspensions without surfactant. Even at $\text{pH} = 3$ the isoelectric point of TiO_2 appears at SDS concentration $\log c_0 = -3.6$ ($2.5 \times 10^{-4} \text{ mol dm}^{-3}$) while at $\text{pH} = 6$ it occurs at $10^{-4} \text{ mol dm}^{-3}$ SDS. Moreover, at the SDS concentration higher than $5 \times 10^{-4} \text{ mol dm}^{-3}$ at both pH values (3 and 6) the negative zeta potential is practically the same, while in the system without SDS the zeta potential is positive at these pHs and equals 40 mV and 7 mV, respectively (Figure 4a). The effective diameter maximum and the sedimentation rate coincide very well, but the maxima are shifted toward higher SDS concentrations relative to the respective isoelectric points (Figure 4a,b,c). Moreover, the maxima are pH independent. It is worth noting that the maximal effective diameter of the aggregated TiO_2 particles is bigger at $\text{pH} = 3$ than $\text{pH} = 6$ (Figure 4b) while the sedimentation rate is the same (Figure 4c). If SDS concentration is increased to $5 \times 10^{-3} \text{ mol dm}^{-3}$ at both pH values (3 and 6), all three parameters are equal. Hence, it may be concluded that at SDS concentration higher than $5 \times 10^{-4} \text{ mol dm}^{-3}$, adsorption of its molecules on TiO_2 determines the surface properties of this oxide. It seems that electrostatic repulsions still play an essential role for system stability.

It was found in our earlier paper⁵ that some SDS adsorption took place even on the negatively charged surface of the same origin TiO_2 (Degussa P-25).²³ The adsorption isotherm at $\text{pH} = 3$ fitted the linear part of the Langmuir

isotherm, but a scatter of the adsorption data appeared at natural pH (5.5–6.5) of the suspension. This might be connected with the drastic changes in the particle aggregation in this pH range, as shown in Figures 2 and 3. The adsorbed SDS amount changed from $7.14 \mu\text{mol g}^{-1}$ at initial $\text{pH}_0 = 10.15$ to $68 \mu\text{mol g}^{-1}$ at $\text{pH}_0 = 3.03$ after 4-h equilibration. Moreover, the initial $\text{pH}_0 = 10.15$ decreased as much as to 7.64 for the final value. If the pH_0 was 3.03, then its final value increased to 3.91.⁵ The observed pH shifts suggested hydroxyl ions release in the SDS adsorption process.²³ The data supported ligand exchange as a possible mechanism for SDS adsorption.^{29–31}

Lately, Tkaczenko *et al.*²² studied the influence of ionic and nonionic surfactants on the TiO_2 suspension properties. Using the ATLAS G-3300 anionic surfactant (possessing $-\text{SO}_3^-$ ionic group) they found that its fast adsorption was determined by pH changes as a function

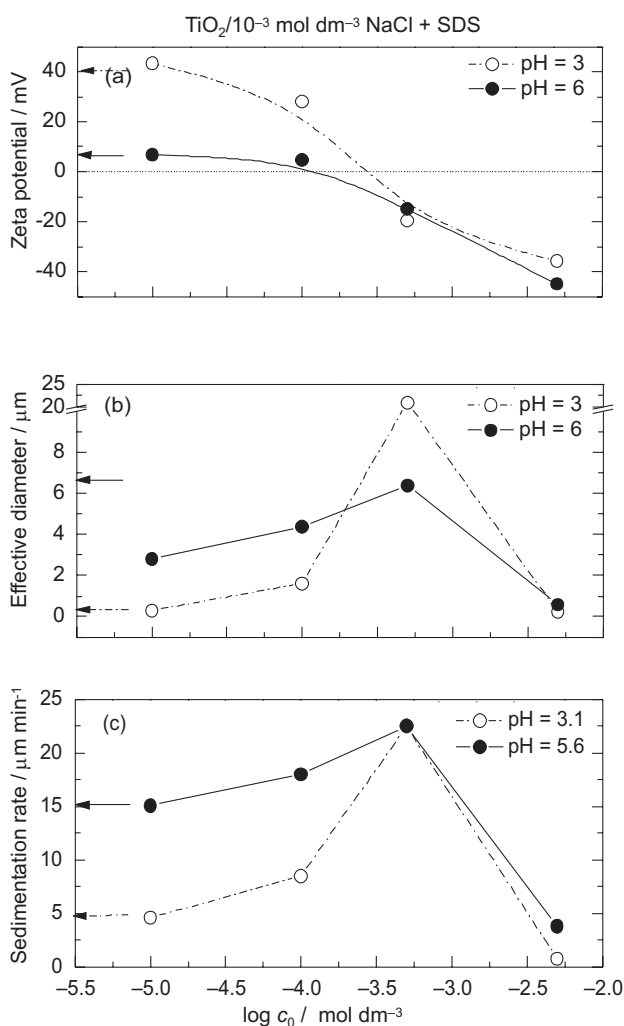


Figure 4. The zeta potential, effective diameter and sedimentation rate of TiO_2 particles in NaCl solution in the presence of SDS at $\text{pH} = 3$ and natural pH as a function of the initial surfactant concentration. Arrows show the respective values in surfactant-free suspensions.

of the surfactant concentration. However, both the zeta potential and particle diameter changed after 6 h equilibration. At *ca.* $10^{-7} \text{ mol dm}^{-3}$ ATLAS concentration, the zeta potential (initially close to zero) increased to about +15 mV (at $\text{pH} = 6$) and a maximum in TiO_2 particle diameter also occurred, *ca.* $4.5 \mu\text{m}$ at $2 \times 10^{-6} \text{ mol dm}^{-3}$. In our study, at this pH and SDS concentration of $5 \times 10^{-4} \text{ mol dm}^{-3}$, the effective diameter of TiO_2 was comparable (Figure 4b). The authors²² suggest that the changes in zeta potential during 6 h suspension equilibration might be due to desorption of the surfactant from the TiO_2 surface.

$\text{TiO}_2/10^{-3} \text{ mol dm}^{-3} \text{ NaCl} + \text{DTAB, TTAB or CTAB}$ Systems

Effects of the three investigated surfactants on the zeta potential, effective diameter and sedimentation rate of TiO_2 suspensions are shown in Figures 5–7. Respective magnitude values determined in reference suspensions without surfactants are marked by arrows in the figures. These surfactants are ammonium salts with an increasing length of the n-alkane chain by $-\text{CH}_2-$ group in each. The presented results were obtained at natural pH of the suspension (6.7–6.8) and regulated to $\text{pH} = 10.0$. As can be seen from the figures, the influence of surfactants depends on their chain length. Analyzing the zeta potential changes, it can be seen that at both pH values of TiO_2 suspension and at the same concentration of TTAB and CTAB, a stronger effect is observed in the presence of CTAB, where the shift towards lower negative values of the zeta potential already appears in $10^{-6} \text{ mol dm}^{-3}$ solution and a reverse of the zeta potential sign (surface charge) from negative to positive takes place in *ca.* $1.8 \times 10^{-5} \text{ mol dm}^{-3}$ CTAB while in the case of TTAB it occurs in $5 \times 10^{-5} \text{ mol dm}^{-3}$ solution. The same is true at $\text{pH} = 10.3$ – 10.5 , where the zeta potential sign reverses in $5 \times 10^{-5} \text{ mol dm}^{-3}$ and $3.2 \times 10^{-4} \text{ mol dm}^{-3}$, respectively (Figures 6 and 7).

In the presence of DTAB, at its concentration of $5 \times 10^{-4} \text{ mol dm}^{-3}$, the zeta potential of TiO_2 at $\text{pH} = 6.7$ and 10.5 is negative (Figure 5a), but it is positive in the presence of TTAB or CTAB. This is depicted in Figures 8 and 9 at the natural suspension pH and $\text{pH} = 10.4$, respectively. At the natural pH of the suspension, the sequence of zeta potential changes is: -20 mV , -7 mV , 25 mV for DTAB, TTAB and CTAB, respectively, while it is 42.5 mV in the reference system (no surfactant). The same sequence at $\text{pH} = 10.4$ is as follows: -41 mV , -25 mV , 5.5 mV and 37 mV . At this pH, the zeta potential changes roughly proportionally to the chain length increase (see Figure 10). In general, concerning zeta potential changes, it is clearly seen from Figures 8 and 9 that the surface activity of cationic surfactants increases with the chain length increase. The influence appears already at their low concentration (10^{-6} – $10^{-5} \text{ mol dm}^{-3}$) both at natural as well as alkaline $\text{pH} = 10.4$, at which

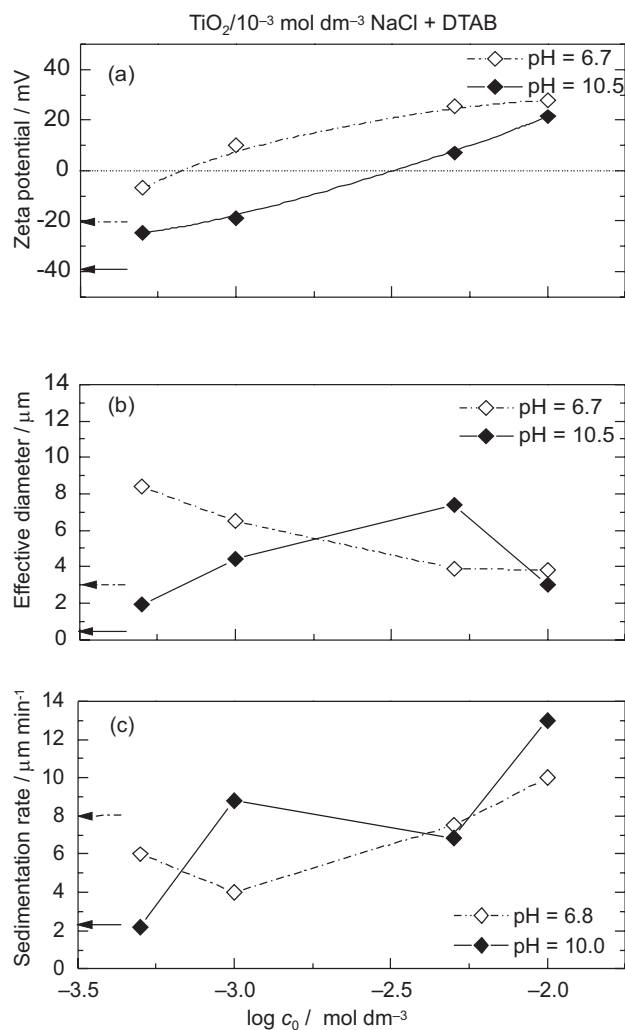


Figure 5. The zeta potential, effective diameter and sedimentation rate of TiO_2 particles in NaCl solution in the presence of DTAB at natural pH and pH = 10–10.5 as a function of the initial surfactant concentration. Arrows show the respective values in surfactant-free suspensions.

TiO_2 surface is significantly negatively charged. The adsorption mechanism and surface activity of surfactants have been described in the literature many times. Two review articles have been published lately.^{24,32} Since concentrations of the surfactants tested in this paper were always below the appropriate c.m.c., adsorption of individual surfactant molecules occurred first. Depending on the surfactant concentration, Atkin *et al.*²⁴ suggest four spans of the adsorption mechanism on oxide surfaces. Below c.m.c., the third one is termed »electrostatic and hydrophobic concentration«, where the adsorption is driven both by electrostatic attraction and hydrophobic interactions. They called referred to the adsorbed morphology as 'teepee' structure, where the overall surface charge is neutralized, but there is a positive charge at the interface because of the aggregation of surfactant molecules (surface micelles). Actually, the state of the oxide sur-

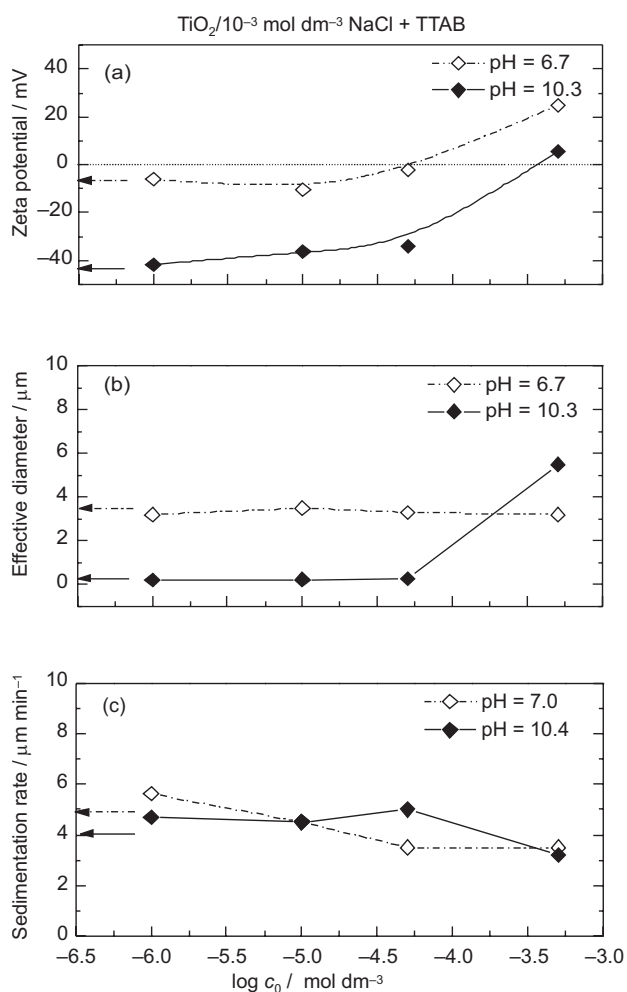


Figure 6. The zeta potential, effective diameter and sedimentation rate of TiO_2 particles in NaCl solution in the presence of TTAB at natural pH and pH = 10.3 as a function of the initial surfactant concentration. Arrows show the respective values in surfactant-free suspensions.

face in the fourth span is the same as in the third one but, instead of individual molecules, the micelles adsorb, because the adsorption involves concentrations above c.m.c.

In the case of the results presented in Figures 7–9, it may be conducted that after the first two spans at lower surfactant concentrations, *i.e.*, the electrostatic concentration span, and the electrostatic and hydrophobic concentration span, the hydrophobic concentration span ends the adsorption process appearing in conversion of the zeta potential from a negative to a positive one.

However, the changes in the effective diameter and sedimentation rate, shown in Figures 5–7, caused by these three cationic surfactants are not easy to interpret in relation to the zeta potential changes. Despite the electrostatic repulsion, hydrophobic (dispersion) n-alkane chain-chain interactions have also to be considered, as well as steric stabilization. In the case of CTAB possessing the

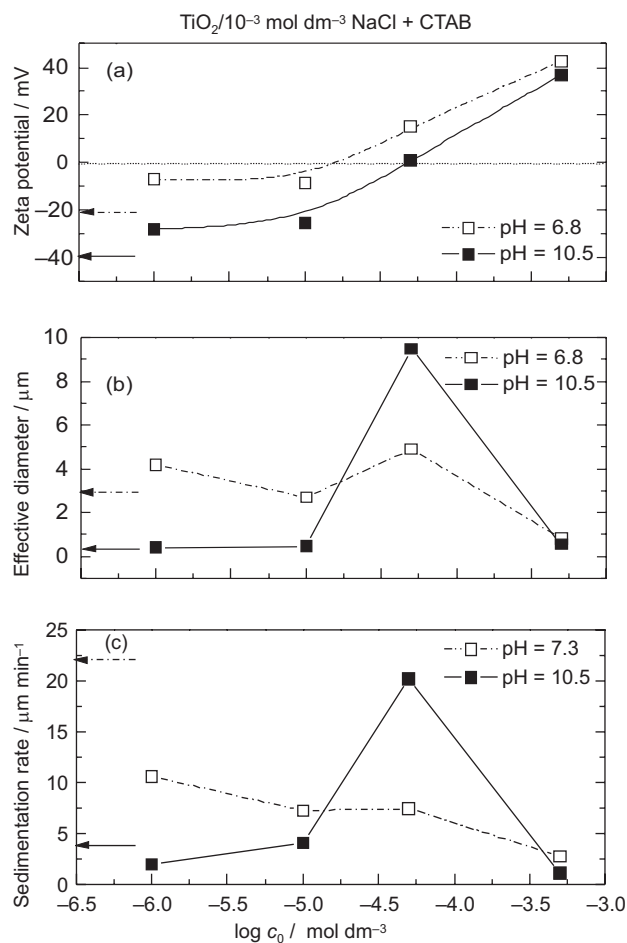


Figure 7. The zeta potential, effective diameter and sedimentation rate of TiO_2 particles in NaCl solution in the presence of CTAB at natural pH and pH = 10.5 as a function of the initial surfactant concentration. Arrows show the respective values in surfactant-free suspensions.

longest chain, both the effective diameter and the sedimentation rate correlate quite well with the zeta potential changes (Figure 7), especially at pH = 10.5, where the maxima of the diameter and sedimentation rate correlate very well with the zero zeta potential. Shorter by the $-\text{CH}_2-$ group, TTAB surprisingly does not affect these two quantities (Figure 6), which in the whole concentration range are close to those in the surfactant free system. Only at the highest concentration of $5 \times 10^{-4} \text{ mol dm}^{-3}$ and pH = 10.4, a significant increase in the particle size (from *ca.* $0.3 \mu\text{m}$ to $5.8 \mu\text{m}$) is observed (Figure 6b). But at this concentration, no decrease in the diameter is observed at pH = 6.7, though the zeta potential increases from *ca.* 0 mV to +25 mV. In the presence of this surfactant, the sedimentation rate is both pH and concentration (10^{-6} – $5 \times 10^{-4} \text{ mol dm}^{-3}$) independent.

In DTAB solutions, whose concentrations were higher than those of TTAB and CTAB (except for one of $5 \times 10^{-4} \text{ mol dm}^{-3}$), the changes in the effective diameter of TiO_2 particles correlate with the zeta potential changes (Fig-

ures 5a and 5b). At pH = 10.5, a maximum ($7.3 \mu\text{m}$) is observed where the zeta potential is close to zero. At the natural pH = 6.7, decreasing effective diameter is observed with the increasing zeta potential, whose values are higher than those at pH = 10.5. However, changes in the sedimentation rate are not clear in relation to the zeta potential changes. At pH = 6.8, a minimum is observed in $10^{-3} \text{ mol dm}^{-3}$ DTAB solution, where the zeta potential is small, *ca.* +10 mV. In contrast, in $10^{-2} \text{ mol dm}^{-3}$ solution (which is below but close to c.m.c.²⁴), the zeta potential amounts to *ca.* 28 mV and the sedimentation rate is maximal, $10 \mu\text{m min}^{-1}$, but not much faster than in the surfactant free solution ($8 \mu\text{m min}^{-1}$), where the zeta potential is -20 mV (Figure 5c). The sedimentation rate at pH = 10.0 is even less clear in relation to the zeta potential changes. It is the fastest in $10^{-2} \text{ mol dm}^{-3}$ DTAB solution. These results show that in the presence of this surfactant, the principal factor determining the TiO_2

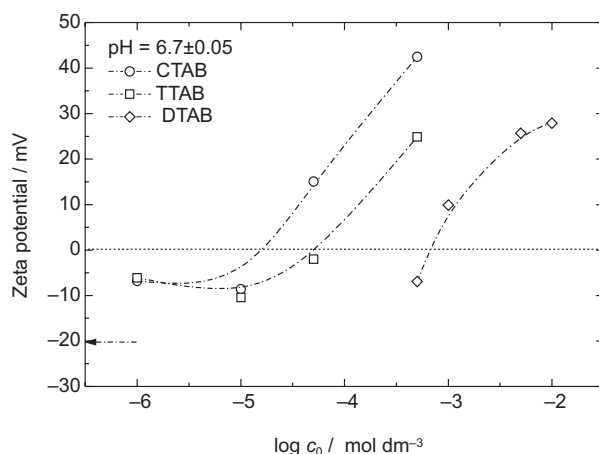


Figure 8. The zeta potential of TiO_2 particles in NaCl solution in the presence of the three cationic surfactants at natural pH as a function of the initial surfactant concentrations. The arrow shows the value in surfactant-free suspensions.

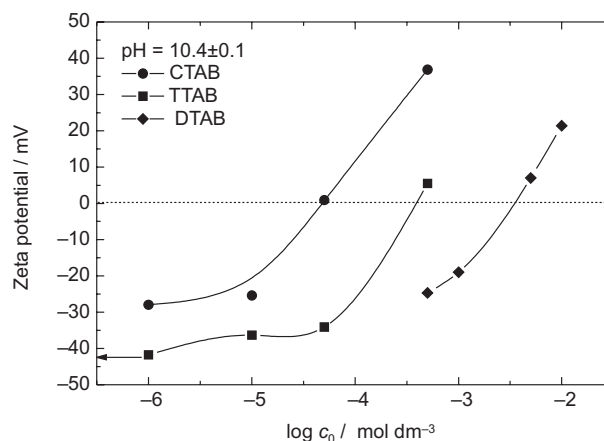


Figure 9. The zeta potential of TiO_2 particles in NaCl solution in the presence of the three cationic surfactants at pH ≈ 10.4 as a function of the initial surfactant concentrations. The arrow shows the value in surfactant-free suspensions.

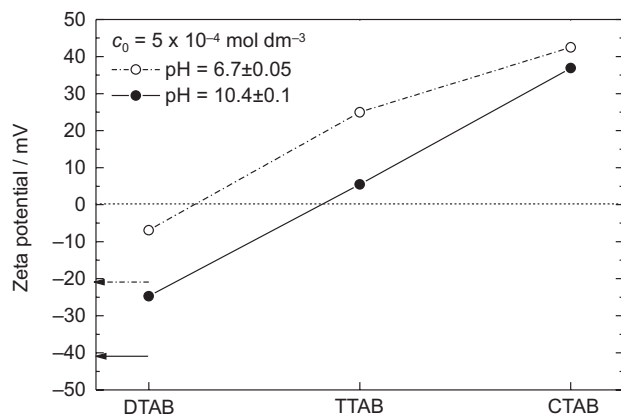


Figure 10. Influence of the alkyl chain length of cationic surfactants ($5 \times 10^{-4} \text{ mol dm}^{-3}$) on the zeta potential of TiO_2 particles in NaCl solution at natural pH and $\text{pH} \approx 10.4$. Arrows show the respective values in surfactant-free suspensions.

suspension stability is its concentration. At the highest concentration ($10^{-2} \text{ mol dm}^{-3}$), the sedimentation process may be driven by hydrophobic interaction of dodecyl alkaline chains. However, as we have not determined the surfactants adsorption, a more detailed picture of the interface would be too speculative. Adsorption experiments will be conducted next.

$\text{TiO}_2/10^{-3} \text{ mol dm}^{-3} \text{ NaCl} + \text{DPPC}$ System

We have performed some preliminary experiments using lecithin as a suspension stabilizer. Replacement of a synthetic surfactant with a natural one in some dispersion would be of practical meaning.³³ The experiments were conducted in the presence of 5 mg dm^{-3} and 10 mg dm^{-3} of DPPC. At $\text{pH} = 3$ or 10 , no significant influence on the TiO_2 suspensions was observed. However, some effects were visible at natural $\text{pH} = 5.9\text{--}6.1$. The results are presented in Figure 11. As little as 5 mg dm^{-3} of DPPC causes an increase of the negative zeta potential from -5 mV to -16 mV . It is accompanied by a decrease in the effective diameter from *ca.* $5 \mu\text{m}$ to $3 \mu\text{m}$. However, only a very slight decrease in the sedimentation rate is observed. Moreover, a double increase in DPPC content from 5 mg dm^{-3} to 10 mg dm^{-3} causes a decrease of the negative zeta potential to -10 mV , no change in the diameter, and a significant increase in the sedimentation rate from $15 \mu\text{m min}^{-1}$ to $27 \mu\text{m min}^{-1}$. In further studies of this system, more DPPC concentrations will be used. It could also be interesting to study the suspension properties in the presence of Ca^{2+} ions. Since the lecithin molecule possesses two ions separated by two methylene groups, two ionic forms may appear. In one of them, the charges are at a maximal distance, and in the other, the separa-

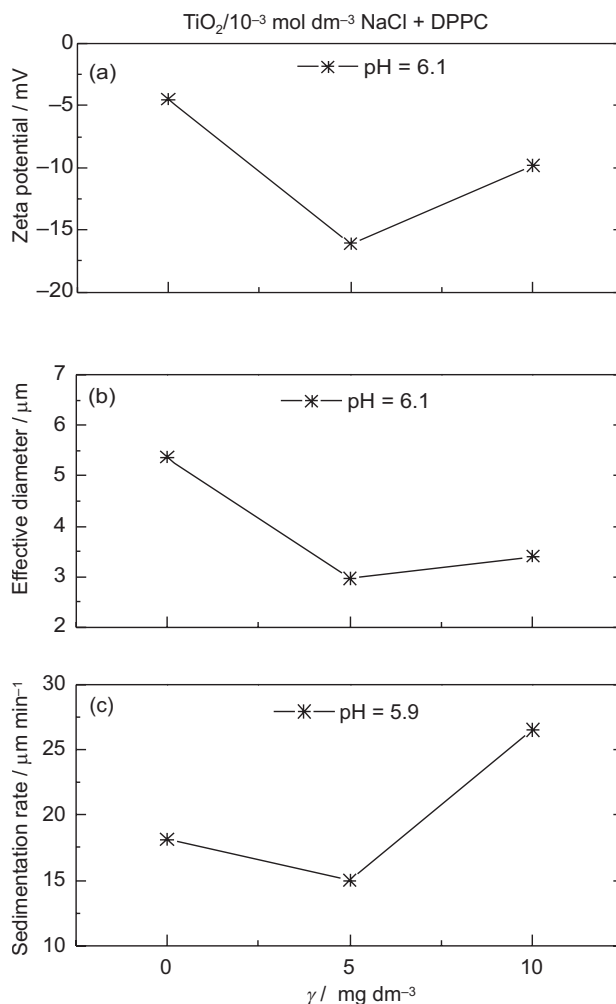


Figure 11. The zeta potential, effective diameter and sedimentation rate of TiO_2 particles in NaCl solution in the presence of DPPC at the natural pH of the suspension.

tion distance is reduced due to an internal linkage between phosphate and trimethylammonium groups.³⁴ This linkage is weakened by increasing the electrolyte concentration. Moreover, it appears that Ca^{2+} is more effective than Na^+ .³⁴ In the lecithin monolayer on the electrolyte subphase, calcium ions can be located in an upper position between two oxygen atoms, which are partially negatively charged. This is also caused by the repulsion originating from the $(\text{CH}_3)_3\text{N}^+$ group.³⁴ In the light of what has been said, one may expect more significant effects of the DPPC presence on the TiO_2 suspension stability if Ca^{2+} ions are also present. Such experiments will be conducted next.

Acknowledgement. – The authors highly appreciate the financial support of the Polish Ministry of Science and Higher Education. Projects: WCh/BStat/3 and Project No. N204 128 32/3188.

REFERENCES

1. T. Preočanin and N. Kallay, *Croat. Chem. Acta* **79** (2006) 95–106.
2. W. Janusz, in: P. Hsu (Ed.), *Electrical Double Layer at the Metal Oxide/Electrolyte Interface*, in: *Surfactant Science Series*, vol. 85, Dekker, New York, 1999, pp. 135–206.
3. M. Kosmulski, *Chemical Properties of Materials*, in: *Surfactant Science Series*, vol. 102, Dekker, New York, 2001, pp. 88–170.
4. M. Kosmulski, *Adv. Colloid Interface Sci.* **99** (2002) 255–264.
5. L. Yezek, R. L. Rowell, L. Holysz, and E. Chibowski, *J. Colloid Interface Sci.* **225** (2000) 227–232.
6. M. Kosmulski and E. Matijević, *Colloids Surf.* **64** (1992) 57–65.
7. W. Janusz, *Polish J. Chem.* **68** (1994) 1871–1880.
8. R. Sprycha, *J. Colloid Interface Sci.* **102** (1984) 173–185.
9. M. Kosmulski, S. Durand-Vidal, J. Gustafson, and J. B. Rosenholm, *Colloids Surf., A* **157** (1999) 245–259.
10. M. Arellano, I. Manas-Zloczower, and D. L. Feke, *Powder Technol.* **84** (1995) 117–126.
11. E. Sahle-Demessie, M. Gonzalez, Z. M. Wang, and P. Biswas, *Ind. Eng. Chem. Res.* **38** (1999) 3276–3284.
12. Y. Chen, J. C. Crittenden, S. Hackney, L. Sutter, and D. W. Hand, *Environ. Sci. Technol.* **39** (2005) 1201–1208.
13. H. Maskrot, N. Herlin-Boime, Y. Leconte, K. Jursikova, C. Reynaud, and J. Vicens, *J. Nanopart. Res.* **8** (2006) 351–360.
14. H. S. Jung, S-W. Lee, J. Y. Kim, K. S. Hong, Y. Ch. Lee, and K. H. Ko, *J. Colloid Interface Sci.* **279** (2004) 479–483.
15. J. Yu, J. C. Yu, and X. Zhao, *J. Sol-Gel Sci. Technol.* **24** (2002) 95–103.
16. A. Salvador and A. Chisvert, *Anal. Chem. Acta* **537** (2005) 1–14.
17. J. Schulz, H. Hohenberg, F. Pflücker, E. Gärtner, T. Will, S. Pfeiffer, R. Wepf, V. Wendel, H. Gers-Barlag, and K.-P. Wittern, *Adv. Drug Delivery Rev.* **54** (2002) S157–A163.
18. K. Megoro, T. Adachi, R. Fukunishi, and K. Esumi, *Langmuir* **4** (1988) 1160–1162.
19. I. A. Polunina, S. S. Mikhailova, A. A. Isirikyan, and N. S. Ovchinnikova, *Colloids Surf., A* **105** (1995) 159–165.
20. K. Esumi, K. Sakai, K. Torigoe, T. Suhara, and H. Fukui, *Colloids Surf., A* **155** (1999) 413–417.
21. K. Esumi, *Colloids Surf., A* **176** (2001) 25–34.
22. N. H. Tkachenko, Z. M. Yaremko, C. Bellmann, and M. M. Soltys, *J. Colloid Interface Sci.* **299** (2006) 686–695.
23. X. Chen, H. Cheng and J. Ma, *Powder Technol.* **99** (1998) 171–176.
24. R. Atkin, V. S. J. Craig, E. J. Wanless, and S. Biggs, *Adv. Colloid Interface Sci.* **103** (2003) 219–304.
25. http://www.turbiscan.com/home/lab_present1.htm
26. W. Janusz and M. Matysek, *J. Colloid Interface Sci.* **296** (2006) 22–29.
27. N. Kallay, T. Madić, K. Kučej, and T. Preočanin, *Colloids Surf., A* **230** (2003) 3–11.
28. A. Foissy, A. M. M'Pandou, and J. M. Lamarche, *Colloids Surf.* **5** (1982) 363–368.
29. C. E. Giacomelli, M. J. Avena, and C. P. De Pauli, *Langmuir* **11** (1995) 3483–3490.
30. T. Hiemstra, W. H. Van Riemsdijk, and G. H. Bolt, *J. Colloid Interface Sci.* **133** (1989) 91–104.
31. T. Hiemstra, J. C. M. De Witt, and W. H. Van Riemsdijk, *J. Colloid Interface Sci.* **133** (1989) 105–117.
32. D. W. Fuerstenau and Pradip, *Adv. Colloid Interface Sci.* **114–115** (2005) 9–26.
33. S. Pastewski, K. Medrzycka, and J. Zimoch, *Przem. Chem.* **84/5** (2205) 345–349.
34. D. O. Shah and J. H. Schulman, *J. Lipid Res.* **8** (1967) 227–233.

SAŽETAK

Utjecaj ionskih surfaktanata i lecitina na stabilnost titanijeva dioksida u vodenoj otopini elektrolita

Emil Chibowski, Lucyna Holysz, Konrad Terpilowski i Agnieszka Ewa Wiacek

Proučavani su zeta potencijal, efektivni promjer i brzina sedimentacije suspenzije TiO₂ (Degussa P-25) u prisutnosti NaCl i anionskog (natrijev dodecilsulfat, SDS) ili kationskih (dodeciltrimetilamonijev bromid, DTAB; tetradeziltrimetilamonijev bromid, TTAB; i heksadeziltrimetilamonijev bromid, CTAB) surfaktanata, kao i lecitina (1,2-dipalmitoil-*sn*-glicero-3-fosfokolin, DPPC). U pokusima su mijenjani koncentracija surfaktanata (lecitina) i pH otopina. Dobiveni rezultati pokazuju značajan utjecaj surfaktanata na mjerene veličine. Ovisno o koncentraciji surfaktanata i pH, oni stabiliziraju ili destabiliziraju suspenziju. Anionski surfaktant SDS je učinkovitiji u usporedbi s kationskim surfaktantima korištenim u procesima stabilizacije/destabilizacije suspenzije. Lecitin (DPPC), u upotrijebljenim koncentracijama, utječe na parametre samo pri prirodnom (ne podešenom) pH suspenzije. Pri koncentraciji od 5 mg dm⁻³ on stabilizira suspenziju TiO₂, dok se pri koncentraciji od 10 mg dm⁻³ pojavljuju neki destabilizacijski efekti u odnosu na suspenziju bez DPPC.