

# Stability of manganese dioxide by guar gum in the absence or presence of surfactants

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**Abstract** Stability of the manganese dioxide ( $\text{MnO}_2$ ) suspensions by non-ionic guar gum (GG) in the absence or presence of the surfactants: anionic sodium dodecyl sulphate (SDS), cationic hexadecyltrimethylammonium bromide (CTAB) and non-ionic Triton X-100 (*t*-octylphenoxypolyethoxyethanol) and their equimolar mixtures (SDS/TX-100; CTAB/TX-100) was measured using turbidity. The obtained results of the manganese dioxide suspensions stability were discussed together with the adsorption data and with the data concerning the thicknesses of the adsorption layers. In order to gain more information about the structure of the electric double layer surface charge density and the zeta potential measurements were performed. The obtained results show that the addition of guar gum to the  $\text{MnO}_2$  suspensions increases  $\text{MnO}_2$  stability. The larger this increase is, the higher is the concentration of the polymer (concentration range 10–200 ppm). Moreover, the addition of single surfactants also causes the increase in the effectiveness of stabilizing the manganese dioxide suspensions. The reason for that is formation of multilayer complexes between the polymer and the surfactants. In such a system both the adsorption of polymer and the

thickness of polymer adsorption layer increase. The greatest increase in the stability of  $\text{MnO}_2$ /GG suspensions was provided by the mixture of anionic and non-ionic surfactants due to a strong synergistic effect. Also, mixing the polymer and two surfactants reduces the stability of the suspension.

**Keywords** Stability of colloids · Guar gum  
SDS CTAB TX-100 · Manganese dioxide

## Introduction

Colloidal dispersions find many interesting applications in different branches of industry (Napper 1983). However, the problem of such systems is their stability. The theory proposed by Derjaguin, Landau (1941), Verwey and Overbeek (1948) (DLVO theory) considers the stability of colloidal dispersion using the net interaction energy ( $V$ ) given by the algebraic sum of negative contribution due to the London-Van der Waals attraction ( $V_A$ ) and a positive one due to the electrostatic repulsion ( $V_R$ ); ( $V = V_A + V_R$ ). Because  $V_R$  is very sensitive to the electrolyte concentration ( $V_A$  is not), the stability of colloidal dispersion can be controlled by the ionic strength of background electrolyte added to the dispersion. The electrolyte has the ability to screen repulsive forces. Aqueous dispersion of solid particles can be electrostatically stabilized even without a polymer. Such a situation occurs if the range of the electrostatic repulsion is higher than that

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of the attractive Van der Waals forces. The colloidal dispersions in nonpolar solvents are usually unstable in the absence of polymers. In polar and apolar solvents the colloidal dispersions can be sterically stabilized by polymers which adsorb on the surface of the solids. However, natural or synthetic high molecular weight substances, because of their high interfacial activity, can stabilize or flocculate the colloidal suspensions. Increase or decrease of stability depends on the molecular weight of polymer and on its concentration (Wiśniewska et al. 2013). In some applications flocculation is desired, for example in purification of water suspensions and papermaking industry or mineral processing, but in majority of cases polymers are added to the colloidal dispersion to induce the increase of stability. Stable colloids are needed in ceramics, food, cosmetics, drugs, paints and varnishes (Napper 1983). Colloid stability is observed when the polymer layer created on the surface of a solid is thinner than the electric double layer and then the adsorbed polymer adopts a tethered brush structure (Ouali et al. 1999). Aggregation of particles of a solid covered by a polymer is induced by formation of interparticle links especially when the adsorbed polymer creates a loop structure (Ouali et al. 1999).

In most cases polymers are added to the colloidal dispersion in order to induce stability or flocculation but recently mixtures of polymers and surfactants have been used more widely (Somasundaran et al. 1998; Fan et al. 1999; Terayama et al. 2001; Besra et al. 2002; Şakar-Deliormanlı 2007). The first reason for that is higher effectiveness of the polymer-surfactant mixtures especially in stabilization of drug particles. The second is the fact that the desired polymer conformation can be influenced by the addition of the second polymer or surfactant as well as changing pH, ionic strength or type of electrolyte. It is generally known that the adsorption in the systems where not only a polymer but also a surfactant is present depends on the chemical character of these two adsorbates as well as on the properties of the solid surface (Grządka 2011). In the systems where a polymer and the surface active agents are present three adsorption cases can be distinguished: (1) competitive adsorption: both the polymer and surfactant have the affinity for the surface but not for each other (2) complex formation: only one of these two substances has the affinity for the surface but they can bind each other (3) competitive adsorption together with complex formation: both the

polymer and the surfactant have the affinity for the surface and to each other (Grządka 2011). The stability of the colloidal suspensions may be estimated by many different methods as for example sedimentation rate, electron microscopy, photon correlation spectrometry, particle counting, electron spin resonance, turbidity, spectrophotometry, potentiometric titration and zeta potential measurements (Somasundaran et al. 1998; Wiśniewska et al. 2010, 2012a, b, 2013). Somasundaran et al. (1998) studied the role of conformation and orientation of surfactants and polymers in controlling flocculation and dispersion of aqueous and non-aqueous (toluene)  $\text{Al}_2\text{O}_3$  suspensions. They found that in the aqueous systems the surfactant adsorption generates hydrophobic patches and imparts sufficient hydrophobicity to the particles, but in organic media, where the surface aggregation is not observed, higher surface coverages are required to obtain sufficient hydrophobicity. Moreover, in non-polar systems the stability can also result from the presence of trace polar impurities, such as water, that can induce ionization in the adsorbed layer. Fan et al. (1999) studied competitive adsorption of anionic surfactant (SDS) and anionic polymer (polyacrylic acid) on alumina particles as well as the stability of these suspensions with the particular attention to the conformation of the polymer. They found that the sequence of addition is of crucial importance in determining the dispersion/flocculation of this system. When SDS was added first, both PAA conformation and suspension stability varied with the SDS concentration. Whereas PAA was added first, SDS macromolecules had no effect on the polymer conformation and suspension stability. Terayama et al. (2001) found that the mixture of SDS and cellulose provides more stable aqueous dispersion of CT112 (5-(3-ethoxy-4-pentyloxyphenyl)-2,4-thiazolidinedione) than SDS or cellulose alone. These results were obtained using a turbiscan MA2000. According to these scientists, the steric hindrance was caused by the adsorption of polymer as well as the electrostatic repulsion was caused by the adsorption of SDS. Besra et al. (2002) studied flocculation and dewatering of kaolin suspensions by anionic polyacrylamide in the presence of surfactants (SDS, CTAB, TX-100). They stated that the simultaneous addition of PAM either with SDS or Triton X-100 increases the settling rate, whereas when added from its mixture with CTAB it decreases. The reason is the electrostatic interaction and binding of

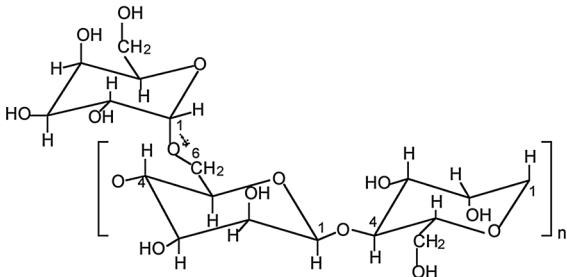
CTAB to PAM-A leading to complex formation, which reduces its flocculating properties. Esumi et al. (2000) studied flocculation of alumina in the presence of the mixture of anionic and nonionic surfactants. They noticed that for the dual systems enhancement of the adsorption of one surfactant would occur by the adsorption of another one. Şakar-Deliormanlı (2007) investigated the effect of cationic surfactant (dodecylamine) and nonionic triblock copolymer (PEO–PPO–PEO) on the dispersion and flocculation behaviour of aqueous silica suspensions and stated that these processes depend on the type and concentration of surfactant surfactant/polymer ratio and surfactant addition sequence to the system.

The aim of this work was to investigate the influence of guar gum and surfactants (anionic SDS, cationic CTAB and nonionic Triton X-100) as well as the mixtures of surfactants (SDS/Triton X-100; CTAB/Triton X-100) on the stability of the MnO<sub>2</sub> suspensions using turbidimetry. The results were

discussed together with the obtained adsorption data, the thicknesses of the guar gum adsorption layer in the presence of surfactants as well as surface charge density and the zeta potential.

Guar gum (GG) is a natural, nonionic, non-toxic polysaccharide, produced from the seeds of the two annual leguminous plants, *Cyamopsis tetragonolobus* and *C. psoraloides* (Ma and Pawlik 2007). This polymer contains the units of  $\beta$ -D-mannopyranose with  $\alpha$ -D-galactopyranose ones linked in the position (1  $\rightarrow$  4) and connected to the mannose backbone through (1  $\rightarrow$  6) glycosidic linkages (Table 1). Polymannose is randomly substituted with galactose. The degree of substitution of polymannose varies from 1.8 to 1.0 (Ma and Pawlik 2005). The average molecular weight of guar gum changes from 1 to 2 million (Cheng et al. 2002). Guar gum is used as a depressant for hydrophobic gangue minerals in flotation of nickel and platinum bearing ores (Wang et al. 2005) or as a blinder of water-insoluble slimes in potash flotation

**Table 1** Names and structures of polymers used in the measurements

Name	Chemical name	Chemical structure
GG	guar gum	
SDS	sodium dodecylsulfate	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_2\text{Na}^+$
CTAB	hexadecyltrimethylammonium bromide	$\left[ \text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3 \right] \text{Br}^-$
Triton X-100	<i>t</i> -octylphenoxypoly-ethoxyethanol	$\text{C}_8\text{H}_{17}\text{-C}_6\text{H}_4\text{-}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ <p style="text-align: right;"><i>n</i>~9.5</p>

(Wiśniewska et al. 2012a). Manganese dioxide was used as an adsorbent. Its chemical inertness, insolubility in water, stability in a broad pH range and well-defined interface allow to use this compound as an adsorbent in many adsorption processes. It occurs in nature as a mineral pyrolusite. This oxide finds application in the production of matches, in glass-making industry for decolourization of glass and as a depolarizer in voltaic cells (Trzebiatowski 1979). Sodium dodecyl sulphate (SDS) ( $C_{12}H_{25}SO_4Na$ ) was used as an anionic surfactant. It is applied in industrial products including engine degreasers, car wash soaps as well as in household products such as shampoos, toothpastes and shaving foams (Scheibel 2004). Hexadecyltrimethylammonium bromide (CTAB) was used as a cationic surfactant. Its uses include synthesis of nanoparticles and hair conditioning products (Chakraborty et al. 2006). *T*-octylphenoxypolyethoxyethanol known as Triton X-100 (TX-100) ( $C_8H_{17}C_6H_4(OCH_2CH_2)_n \times OH$ ;  $n \sim 9.5$ ) was used as a nonanionic surfactant in the presented measurements. Triton X-100 is frequently used in stabilization of biochemistry processes (Prete' et al. 2002).

## Experimental

### Materials

$MnO_2$  produced by POCh Gliwice (Poland) was used as an adsorbent. The BET specific surface area for the sample was found to be  $35 \text{ m}^2 \text{ g}^{-1}$ . The particle size distribution of the  $MnO_2$  sample determined with the use of a Malvern Mastersizer 2000, fell entirely in the range from 1.82 to 22.71  $\mu\text{m}$ , with a volume average size of 6.78  $\mu\text{m}$ . The adsorbent was washed with doubly-distilled water until the conductivity of the supernatant was smaller than  $2 \mu\text{Scm}^{-1}$ . The XRD measurements confirmed that  $MnO_2$  was free of impurities.

Guar gum was obtained from Sigma–Aldrich. All guar gum stock solutions were prepared by quickly adding 0.045 g of gum powder into 45 ml of vigorously stirred water and further stirring for 30 min. The solution was refrigerated overnight to ensure complete hydration or dissolution of guar gum and then filtered through filter paper to remove any undissolved impurities.

SDS, CTAB and Triton X-100 were purchased from Fluka. The concentrations of used surfactants

and their mixtures in all measured systems equalled  $10^{-4} \text{ mol dm}^{-3}$ . Such a value prevents from exceeding the critical micelle concentration. For SDS the critical micelle concentration equals  $0.00825 \text{ mol dm}^{-3}$  (Rodríguez-Cruz et al. 2005), for CTAB  $0.00086 \text{ mol dm}^{-3}$  (Xi and Guo 2007) whereas for Triton X-100— $0.00029 \text{ mol dm}^{-3}$  (Rharbi and Winnik 2001). NaCl produced by Fluka was used as the supporting electrolyte.

All experiments were carried out in doubly-distilled water at room temperature ( $\cong 25 \text{ }^\circ\text{C}$ ) because it was proved that the temperature influences the polymer adsorption, electrokinetic properties of the measured system as well as stability of the obtained suspensions (Wiśniewska 2011).

### Methods

#### *Stability measurements*

The measurements of  $MnO_2$  suspension stability in the presence and absence of guar gum as well as surfactants and their mixtures were conducted. The  $MnO_2$  suspension was prepared by the addition of 0.005 g of metal oxide to  $10 \text{ cm}^3$  of a background electrolyte solution ( $10^{-1} \text{ mol/dm}^3$  NaCl). The obtained suspension was subjected to the action of ultrasounds for 3 min. Then, it was moved to a measuring high glass phial which was placed in a measuring thermostated chamber in the device Turbiscan Lab Expert with the cooling module TLab Cooler. This apparatus possesses the electroluminescence diode which emits collimated light beam ( $\lambda = 880 \text{ nm}$ ) passing through the investigated suspension. It has also two synchronized detectors. The transmission detector recorded light passing through the probe at the angle  $0^\circ$  in relation to the incident light direction. The other one is the backscattering detector registering the light scattered at the angle  $135^\circ$ . The device is connected with the computer which stores and processes the data. The obtained data are stored and converted by the computer program. The results are presented in the form of curves which show the intensities of transmission and backscattering as a function of time. The analysed suspension in a glass vial (7 cm long) was placed in a thermostated measurement chamber. The  $MnO_2$  samples with the polymer or with the polymer and surfactants were prepared in an analogous way. A suitable volume of

the stock guar gum solution ensuring the final concentrations 10; 100 or 200 ppm was added after suspension ultrasounding. In the case of the MnO<sub>2</sub> suspension with guar gum and surfactants besides guar gum (concentration 100 ppm) a suitable volume of the starting solution of surfactant (of the concentration 10<sup>-3</sup> mol/dm<sup>3</sup>) was added ensuring the final concentration 10<sup>-4</sup> mol/dm<sup>3</sup>. Each stability measurement was 15 h long (single scans were collected every 15 min). Because the transmission for all samples was higher than 2 %, the stability parameter—the turbiscan stability index (TSI), was calculated from the transmission graphs. This parameter takes into account all single measurements during the experiments and the TSI value is obtained from their averaging. All processes taking place in the sample (including thickness of sediment and clear layer as well as particles settling) were summed up. This parameter was calculated with the special computer program Turbiscan Easy Soft from the following formula:

$$TSI = \sqrt{\frac{\sum_{i=1}^n (x_i - x_{BS})^2}{n - 1}} \quad (1)$$

(2) where  $x_i$ —the average backscattering for each minute of measurement,  $x_{BS}$ —the average  $x_i$ ,  $n$ —the number of scans.

The TSI values change in the range from 0 to 100. The higher the TSI, the more unstable the system is.

#### Adsorption measurements

10 mL of the solution was prepared from the polymer stock solution (GG), electrolyte (NaCl or CaCl<sub>2</sub>), doubly-distilled water and surfactants (SDS, CTAB, TX-100 or their mixture with the molar ratio 1:1). After 15 min (time for complex formation between polysaccharide and surfactant) 0.2 g of manganese dioxide was added to the solutions. pH was adjusted to the desired value using 0.1 mol dm<sup>-3</sup> HCl and 0.1 mol dm<sup>-3</sup> NaOH. The suspension was shaken for 18 h to achieve the adsorption–desorption equilibrium by means of a thermostated stirrer. To determine guar gum adsorption amount, the colorimetric method described by Dubois et al. (1956) was used. 0.05 mL of 80 % phenol and 5 mL of 98 % sulphuric acid were added to 2 mL of supernatant obtained after centrifugation with the speed 14,000 rpm using a high speed

centrifuge (310b Mechanika Precyzyjna). The centrifugation time was 15 min. After 30 min of colour development, the absorbance was measured at a wavelength of 490 nm using a spectrophotometer (Cary 100, Varian Instruments). All measurements were made as triplicates. In this paper the average values are reported. The amount of GG adsorption on the MnO<sub>2</sub> surface was calculated from a calibration curve according to the concentration difference before and after the adsorption tests.

#### Thickness of adsorption layer

The thickness of the polysaccharide adsorption layer ( $\delta$ ) was determined from the viscosity measurements (M'Pandou and Siffert 1987), using a rheometer (CVO 50, Bohlin Instruments). Polysaccharide adsorption on the solid surface causes the increase of the solid particle radius which gives the adsorption layer thickness ( $\delta$ ). It results in the increase of volume fraction ( $\phi_0$ ) of the dispersed solid. Thus the values  $\delta$  were obtained from the dependence:

$$\delta = r \left[ \left( \frac{\phi_p}{\phi_0} \right)^{1/3} - 1 \right] \quad (2)$$

where  $r$ —the radius of the metal oxide particle,  $\phi_p$ —the volumetric fraction in the presence of polymer,  $\phi_0$ —the volumetric fraction in the absence of the polymer.

The Einstein equation connects the volume fraction of dispersed solid with the suspension viscosity in the following way:

$$\frac{\eta}{\eta_0} = 1 + k\phi_0 \quad (3)$$

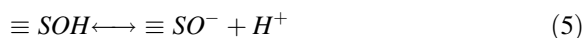
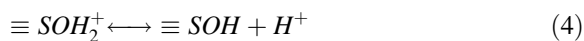
where  $\eta$ —the viscosity of the suspension (Pa s),  $\eta_0$ —the viscosity of the liquid phase (Pa s), and  $k$ —the Einstein coefficient. The coefficient  $k$  is equal to 2.5 for the rigid spherical particles in infinitely diluted suspensions.

The volumetric fraction ( $\phi_p$ ) in the presence of polymer or polymer-surfactant complex was determined from the linear dependence of  $\eta/\eta_0$  versus  $\phi_0$  of manganese dioxide (calibration curve). The viscosity measurements enabling the  $\eta/\eta_0$  ratio determination in the presence of the polymer or the polymer-surfactant complex were made with the volume fraction of MnO<sub>2</sub> equal to  $13.7 \times 10^{-3}$ . Because the adsorption of

polymer or polymer surfactant complex caused the increase of the ratio value,  $\phi_p$  was determined directly from the calibration curve (as a magnitude related to this ratio). Then the thickness of polysaccharide adsorption layer was calculated (Eq. 2).

#### Potentiometric titration

Surface charge on the metal oxide is formed as a result of reactions between the surface hydroxyl groups and the electrolyte ions (Janusz et al. 1997). In aqueous solutions hydrogen/hydroxide ions as well as ions of background electrolyte are the most important in the surface charge formation process. Hydrogen ions influence the surface charge through the acid–base reactions of the surface hydroxyl groups:



In classic theories of the electrical double layer, the background electrolyte ions are assumed to adsorb non-specifically, but in modern models these ions undergo also the specific adsorption.

Comparison of the titration curves of the same ionic strength is used to determine the surface charge density of metal oxide. The surface charge density is calculated from the dependence between the volume of acid/base added to the suspension in order to obtain the desired pH value:

$$\sigma_0 = \frac{\Delta V c F}{m S} \quad (6)$$

where  $\Delta V$ —the dependence between the volume of acid/base added to the suspension in order to obtain the desired pH value,  $c$ —the molar concentration of acid/base,  $F$ —the Faraday constant ( $9.648 \times 10^4 \text{ C mol}^{-1}$ ),  $m$ —the mass of metal oxide,  $S$ —the specific surface area of metal oxide.

$\text{MnO}_2$  surface charge density in the presence and absence of guar gum (10, 100 and 200 ppm) and surfactants (CTAB, TX-100, SDS and mixtures CTAB/TX-100 and SDS/TX-100) was determined using the potentiometric titration method. The NaCl concentration was  $0.1 \text{ mol dm}^{-3}$ . A thermostated, Teflon vessel with a shaker, an automatic burette (Dosimat 665, Methrom) and a pH-meter were the parts of the measurement set. The process was controlled by a computer. The density of  $\text{MnO}_2$  surface

charge was determined using the “Miar\_t” programme written by W. Janusz. The volume of the measured solution was  $50 \text{ cm}^3$ , the mass of the solid 0.2 g. The surface charge density measurements were made as triplicates for every measured system. The results were obtained with the measurement uncertainty lower than 3 %.

#### Zeta potential measurements

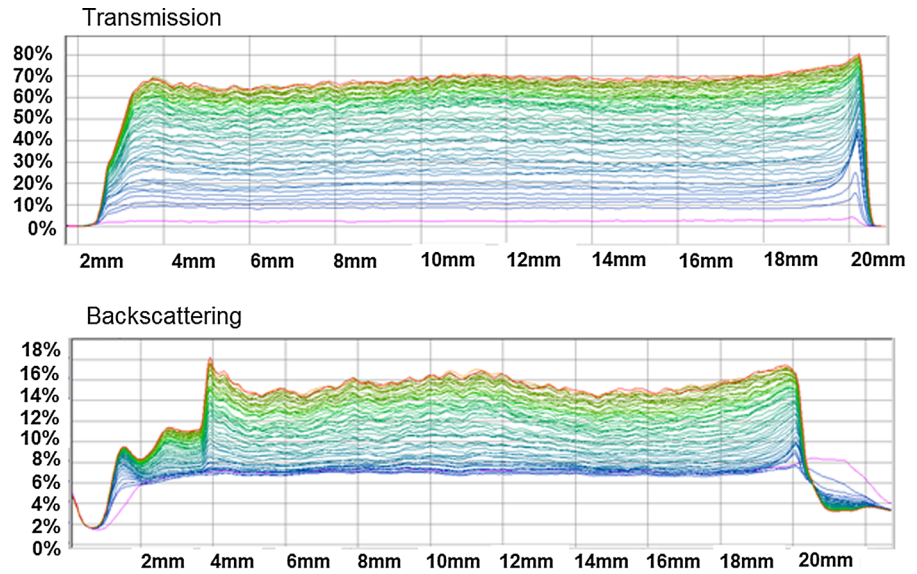
0.05 g of manganese dioxide was added to  $500 \text{ cm}^3$  of the supporting electrolyte solution ( $0.1 \text{ mol dm}^{-3}$  NaCl) with or without GG (10, 100 and 200 ppm) and the surfactants (CTAB, TX-100, SDS and the CTAB/TX-100 and SDS/TX-100 mixtures). The obtained suspensions were ultrasonicated for 10 min. Then pH was adjusted and the electrophoretic mobility was measured using a zetameter (Zetasizer 3,000, Malvern Instruments) and then the zeta potential ( $\zeta$ ) was calculated from the Smoluchowski equation. The zeta potential measurements were made as triplicates and the results were obtained with the measurement uncertainty from 3 to 7 %. In the paper the average values are reported.

## Results and discussion

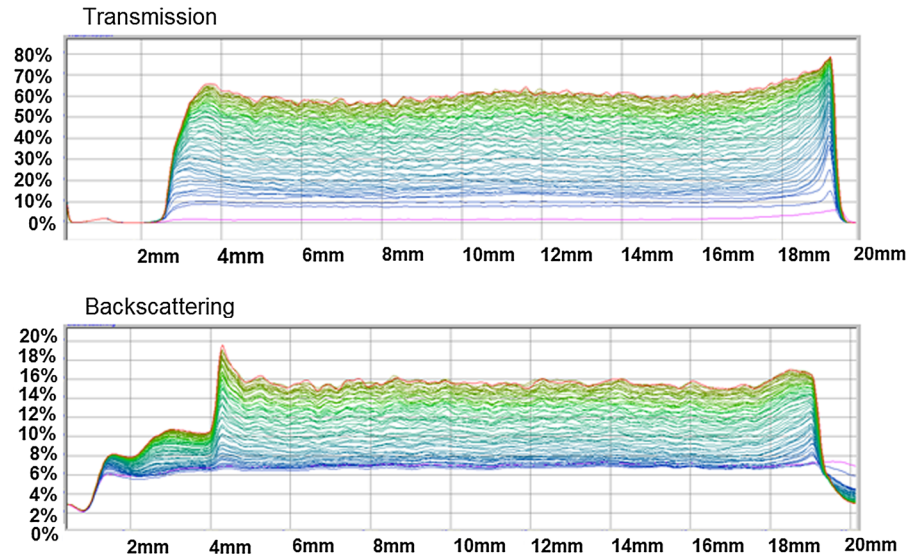
Stabilization-flocculation properties of the suspension in the presence of polymers and surfactants depend on the conformation assumed by macromolecules and surface active compounds adsorbed on the solid surface. It is the conformation that decides about the polymer adsorption and thickness of its adsorption layer. Figures 1, 2, 3, 4, 5, 6, 7, 8, 9 present the dependence of transmission and backscattering of light after its transition through the manganese dioxide suspensions in the absence of guar gum and surfactants (Fig. 1) and in the presence of this polymer (Figs. 2, 3, 4) as well as in the presence of GG, surfactants or their mixtures (Figs. 5, 6, 7, 8, 9). All these results were obtained using Turbiscan. To estimate the total effect of guar gum and surfactants on the stability of  $\text{MnO}_2$  suspension, the stability coefficient (TSI-Turbiscan Stability Index) was determined. The calculated values of TSI are given in Table 2. When the system is less stable the value of the stability coefficient is larger.



**Fig. 1** Transmission and backscattering for the system:  $\text{MnO}_2/0.1 \text{ M NaCl}$ ,  $\text{pH} = 7$



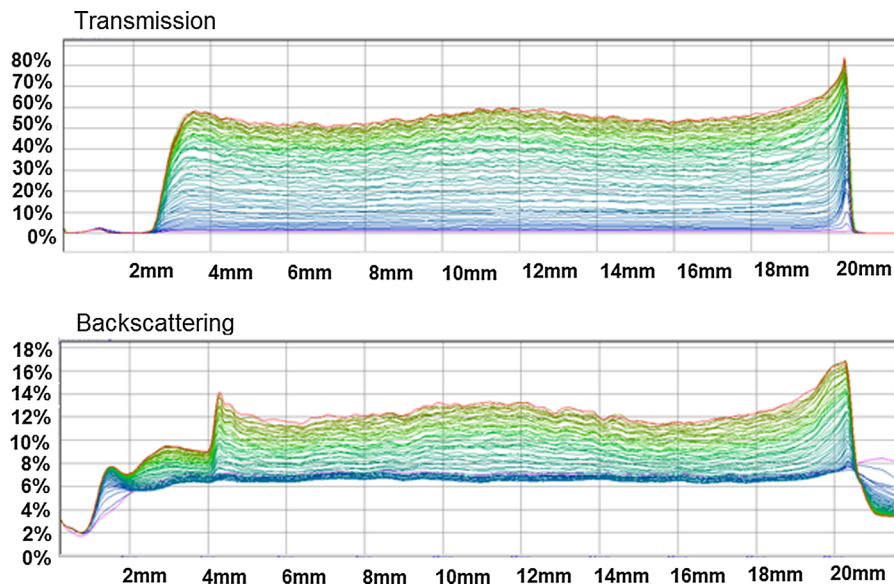
**Fig. 2** Transmission and backscattering for the system:  $\text{MnO}_2/0.1 \text{ M NaCl}/10 \text{ ppm GG}$ ,  $\text{pH} = 7$



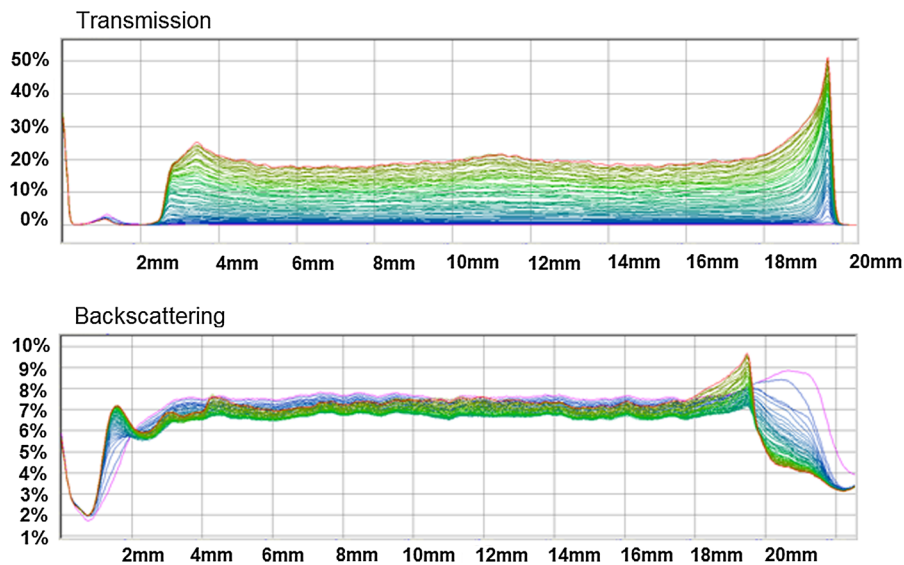
The analysis of the transmission and backscattering curves leads to the conclusion that the  $\text{MnO}_2$  suspension is quite unstable in the absence of polymer or polymer and surfactants (Fig. 1). The evidence for that is the increase of the transmission of the sample from 2 to 70 % in time of the experiment (15 h) as well as the high value (40.32) of the TSI parameter for this system (Table 2). The reason for this instability of the  $\text{MnO}_2$  suspension is the fact that the absolute values of the surface charge density and the zeta potential (Table 3) are much smaller than in the presence of polymer or polymer and surfactants. Then

the repulsive interactions between solid molecules are too weak to provide the stability of the system. Under the measured pH ( $\text{pH} = 7$ ) manganese dioxide surface is negatively charged,  $\text{pH}_{\text{pzc}}$  and  $\text{pH}_{\text{iep}}$  points  $\approx 4.5\text{--}5$  (Grządka 2010). Because of that the metal oxide particles can repel each other (electrostatic stabilization) but this repulsion is too low to achieve the long-last stability. This type of stabilization is based on the mechanism in which the attractive van der Waals forces are counterbalanced by the repulsive Coulomb forces acting between the negatively charged colloidal particles (Sato and Ruch 1980)

**Fig. 3** Transmission and backscattering for the system:  $\text{MnO}_2/0.1 \text{ M NaCl}/100 \text{ ppm GG}$ ,  $\text{pH} = 7$



**Fig. 4** Transmission and backscattering for the system:  $\text{MnO}_2/0.1 \text{ M NaCl}/200 \text{ ppm GG}$ ,  $\text{pH} = 7$

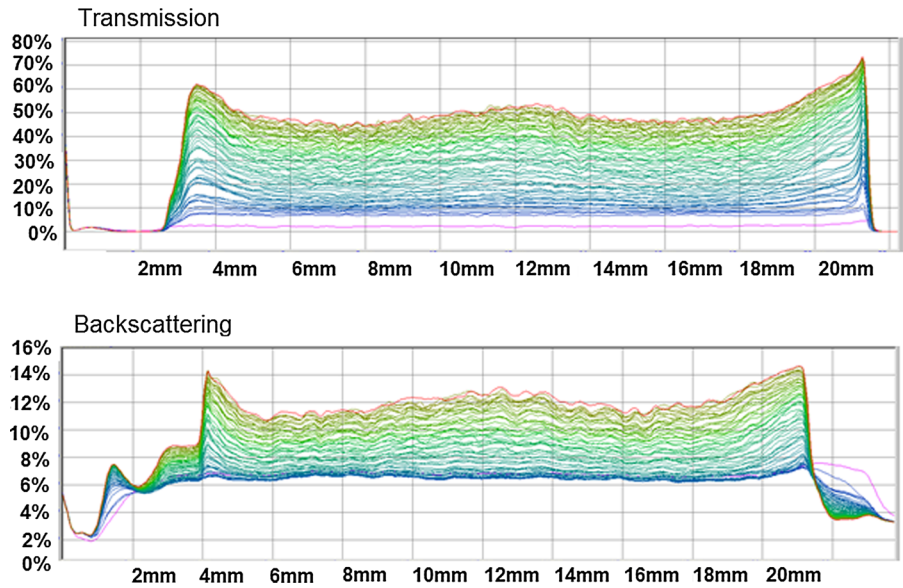


and the particles of metal oxide. They easily fall under the effect of gravity force. The addition of guar gum causes the increase of stability of the  $\text{MnO}_2$  suspensions. The higher polymer concentration, the more stable the  $\text{MnO}_2$  suspensions are. The evidence for this fact are lower transmissions (about 60 % for 10 ppm of GG, about 50 % for 100 ppm of GG and only around 20 % for 200 ppm of GG). Moreover, the TSI values are lower than that in the absence of the polymer. They equal 32.59, 28.54 and 8.38 for 10, 100 and 200 ppm of GG respectively (Table 2). However,

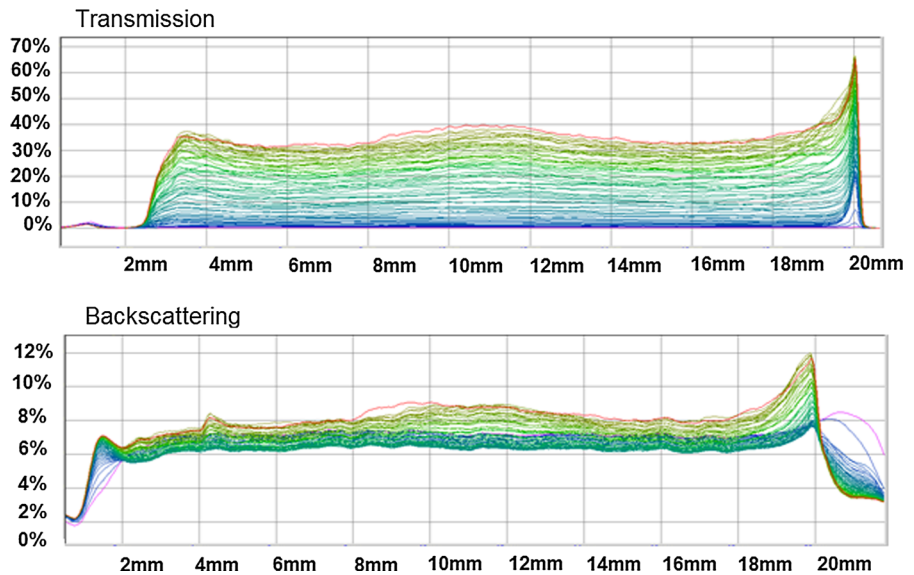
in the case of the system containing 10 ppm of guar gum (Fig. 2), the polymer concentration is too low to provide the stability of the  $\text{MnO}_2$  suspension. Because of low adsorption of GG as well as low value of the adsorption layer thickness (Table 4) polymer poorly covered the manganese dioxide particles and under such conditions the most possible mechanisms are steric and electrostatic stabilizations sometimes called electrosteric stabilization (Napper 1983). The steric stabilization occurs when the polymer chains are adsorbed on a few solid particles and their adsorption



**Fig. 5** Transmission and backscattering for the system:  $\text{MnO}_2/0.1 \text{ M NaCl}/100 \text{ ppm GG}/0.0001 \text{ M CTAB}$ ,  $\text{pH} = 7$



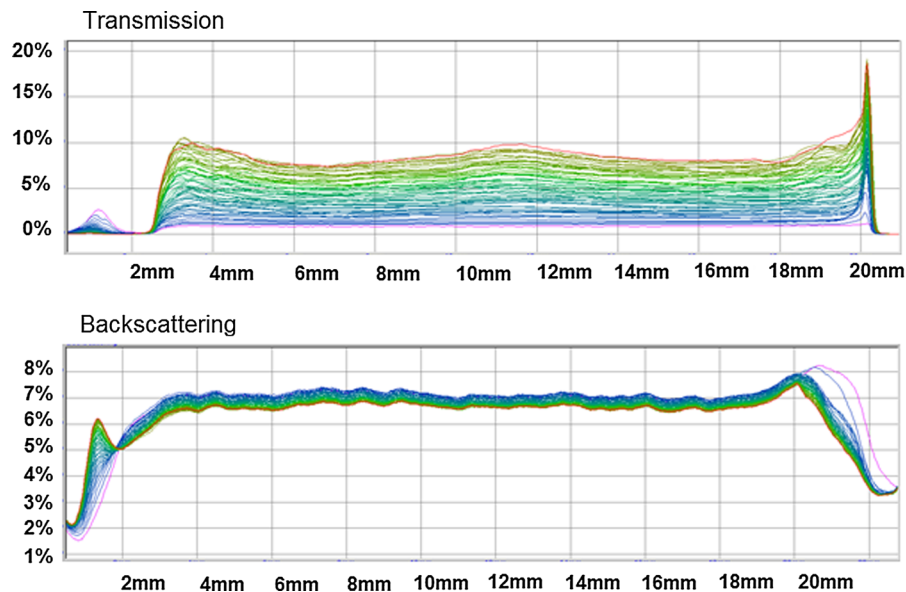
**Fig. 6** Transmission and backscattering for the system:  $\text{MnO}_2/0.1 \text{ M NaCl}/100 \text{ ppm GG}/0.0001 \text{ M TX-100}$ ,  $\text{pH} = 7$



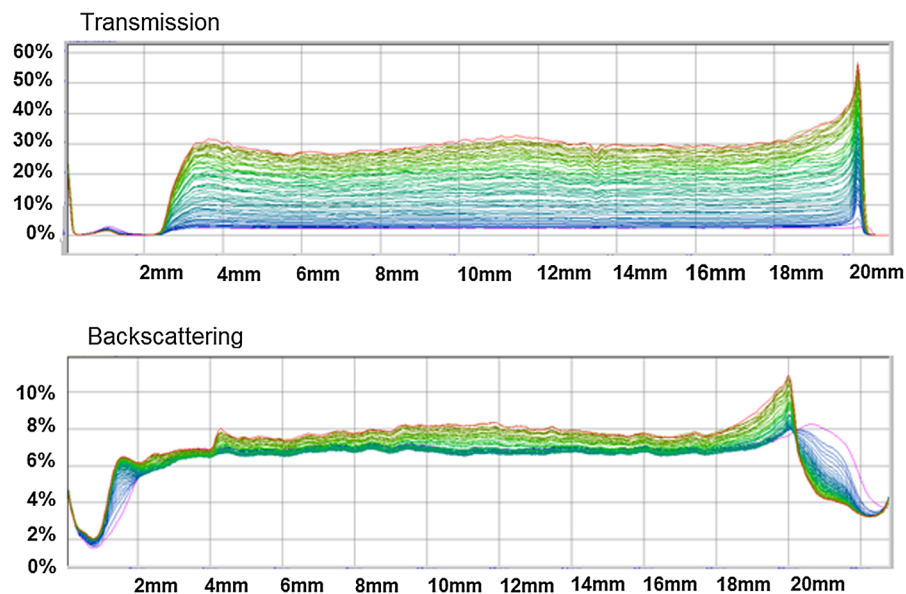
layers can penetrate. This causes the repulsion between the particles, which is the entropic effect. Increasing the concentration of polymer segments in the interpenetrating layers causes the local increase of both the osmotic pressure and the free energy. The consequence of that is the increase in the colloidal stability of the suspensions. In the presence of 100 ppm of guar gum (Fig. 3), the medium stability of the metal oxide suspensions is observed compared to the data obtained for the systems with 10 and 200 ppm of guar gum. These medium results are in

agreement with the values of 100 ppm of guar gum adsorption on  $\text{MnO}_2$  and the thickness created by 100 ppm of GG adsorption layer (Table 4). The highest improvement of the suspension stability occurs in the system containing 200 ppm of GG (Fig. 4). This fact is additionally proved by poor separation of individual scans. In these two cases the most possible mechanism of stabilization is also steric stabilization or combination of steric, electrostatic and depletion stabilization. The last type of stabilization of colloidal suspensions occurs if free polymer

**Fig. 7** Transmission and backscattering for the system:  $\text{MnO}_2$ /0.1 M NaCl/100 ppm GG/0.0001 M SDS, pH = 7



**Fig. 8** Transmission and backscattering for the system:  $\text{MnO}_2$ /0.1 M NaCl/100 ppm GG/0.0001 M mixture CTAB/TX-100, pH = 7

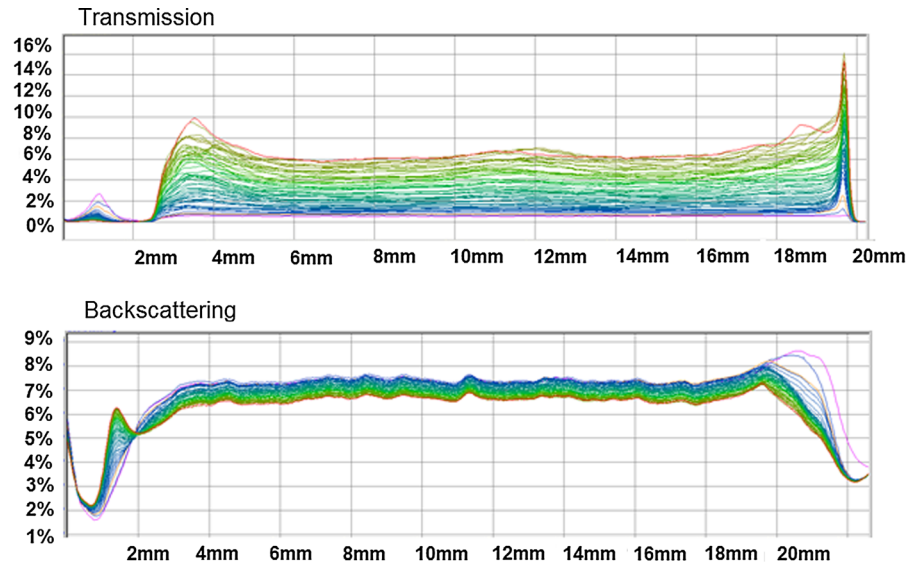


macromolecules which are not adsorbed on  $\text{MnO}_2$  create repulsive forces between the particles, which prevents the solid particles from colloidal aggregation.

The results presented in Figs. 5, 6, 7 enable the analysis of the influence of single surfactants on the stability of manganese dioxide in the presence of 100 ppm of guar gum. As one can notice, the addition of each free measured surfactant (CTAB, TX-100 and SDS) causes the improvement of stability of the 100 ppm guar gum/ $\text{MnO}_2$  system. The TSI values are

lower in the systems with the surfactants in comparison to that containing only 100 ppm guar gum. Moreover, the transmission in the systems with TX-100 and SDS is lower and equals 30 and 10 % respectively and the transmission in the system with CTAB is at the same level as 100 ppm of GG but with the lower TSI value. The adsorption of polysaccharide in the presence of surfactants increases (Table 4) which is the effect of complex formation between these two adsorbates. The nature of these complexes

**Fig. 9** Transmission and backscattering for the system:  $\text{MnO}_2/0.1 \text{ M NaCl}/100 \text{ ppm GG}/0.0001 \text{ M mixture SDS}/\text{TX-100}$ ,  $\text{pH} = 7$



**Table 2** Stability coefficient TSI for the  $\text{MnO}_2$  suspensions in the presence or absence of guar gum and surfactants,  $0.1 \text{ M NaCl}$ ,  $\text{pH} = 7$

System	TSI
$\text{MnO}_2/0.1 \text{ M NaCl}$	40.32
$\text{MnO}_2/0.1 \text{ M NaCl}/10 \text{ ppm GG}$	32.59
$\text{MnO}_2/0.1 \text{ M NaCl}/100 \text{ ppm GG}$	28.54
$\text{MnO}_2/0.1 \text{ M NaCl}/200 \text{ ppm GG}$	8.38
$\text{MnO}_2/0.1 \text{ M NaCl}/100 \text{ ppm GG}/0.0001 \text{ M CTAB}$	23.71
$\text{MnO}_2/0.1 \text{ M NaCl}/100 \text{ ppm GG}/0.0001 \text{ M TX-100}$	15.09
$\text{MnO}_2/0.1 \text{ M NaCl}/100 \text{ ppm GG}/0.0001 \text{ M SDS}$	3.96
$\text{MnO}_2/0.1 \text{ M NaCl}/100 \text{ ppm GG}/0.0001 \text{ M mixture CTAB}/\text{TX-100}$	12.84
$\text{MnO}_2/0.1 \text{ M NaCl}/100 \text{ ppm GG}/0.0001 \text{ M mixture SDS}/\text{TX-100}$	2.89

depends on the chemical character of both the polymer and the surfactants and was discussed in my earlier papers (Grządka and Chibowski 2012; Grządka 2013). What is more, the created adsorption layer in the presence of surfactants is more expanded towards the liquid phase than in the case of the system containing only 100 ppm GG. This observation might be confirmed by the obtained data of the adsorption layer thickness (Table 4). It is also known that the structure of the created complexes is as follows: GG-surfactant-GG-surfactant which means that polysaccharide is directly bonded to the surface of the solid and surfactants molecules are present in the upper parts

**Table 3** Surface charge density ( $\sigma$ ) and the zeta potential ( $\zeta$ ) of manganese dioxide in the presence and absence of guar gum and surfactants,  $0.1 \text{ M NaCl}$ ,  $\text{pH} = 7$

System	Surface charge density ( $\mu\text{C}/\text{cm}^2$ )	Zeta potential (mV)
$\text{MnO}_2/0.1 \text{ M NaCl}$	-18.33	-3.17
$\text{MnO}_2/0.1 \text{ M NaCl}/10 \text{ ppm GG}$	-18.39	-14.78
$\text{MnO}_2/0.1 \text{ M NaCl}/100 \text{ ppm GG}$	-18.42	-24.3
$\text{MnO}_2/0.1 \text{ M NaCl}/200 \text{ ppm GG}$	-18.41	-32.2
$\text{MnO}_2/0.1 \text{ M NaCl}/100 \text{ ppm GG}/0.0001 \text{ M CTAB}$	-18.36	5.27
$\text{MnO}_2/0.1 \text{ M NaCl}/100 \text{ ppm GG}/0.0001 \text{ M TX-100}$	-18.54	-25.9
$\text{MnO}_2/0.1 \text{ M NaCl}/100 \text{ ppm GG}/0.0001 \text{ M SDS}$	-18.41	-29.4
$\text{MnO}_2/0.1 \text{ M NaCl}/100 \text{ ppm GG}/0.0001 \text{ M mixture CTAB}/\text{TX-100}$	-18.45	4.36
$\text{MnO}_2/0.1 \text{ M NaCl}/100 \text{ ppm GG}/0.0001 \text{ M mixture SDS}/\text{TX-100}$	-18.33	-32.6

of the electrical double layer (Grządka 2013). Such a conclusion might be drawn on the basis of the electrokinetic results (Table 3). As one can see the surface charge density of  $\text{MnO}_2$  is more or less the same in the presence of GG and surfactants of different chemical character but the zeta potential (diffused part of the electric double layer) changes dramatically in the presence of different surfactants. This is the

**Table 4** Adsorbed amounts and thicknesses of guar gum adsorption layers on the MnO<sub>2</sub> surface in the presence or absence of surfactants, 0.1 M NaCl, pH = 7

System	$\Gamma$ (mg/m <sup>2</sup> )	$\delta$ (nm)
MnO <sub>2</sub> /0.1 M NaCl/10 ppm GG	0.002	2.3
MnO <sub>2</sub> /0.1 M NaCl/100 ppm GG	0.014	6.9
MnO <sub>2</sub> /0.1 M NaCl/200 ppm GG	0.037	20.1
MnO <sub>2</sub> /0.1 M NaCl/100 ppm GG/ 0.0001 M CTAB	0.057	11.5
MnO <sub>2</sub> /0.1 M NaCl/100 ppm GG/ 0.0001 M TX-100	0.023	13.9
MnO <sub>2</sub> /0.1 M NaCl/100 ppm GG/ 0.0001 M SDS	0.051	16.2
MnO <sub>2</sub> /0.1 M NaCl/100 ppm GG/ 0.0001 M mixture CTAB/TX-100	0.059	19.5
MnO <sub>2</sub> /0.1 M NaCl/100 ppm GG/ 0.0001 M mixture SDS/TX-100	0.062	20.3

evidence that guar gum is directly connected with the surface of the metal oxide and surfactants (linked to polysaccharide) are present in the diffused part of the electrical double layer. From the comparison of the results of the MnO<sub>2</sub> suspensions stability, it is visible that in the presence of cationic CTAB the increase of the stability of the MnO<sub>2</sub>/100 ppm GG system is the smallest among single surfactants, in the presence of nonionic TX-100 its value is medium and it is the highest when anionic SDS is added to the adsorption system. The values of the TSI parameter equal 23.71 in the presence of CTAB, 15.09 in the presence of TX-100 and 3.96 after the addition of SDS to the suspension. As follows the anionic surface active agent has the best effectiveness in the stabilizing polymer/metal oxide suspension, cationic surfactant is less effective whereas nonionic one presents the average properties. The reason for this phenomenon is connected with the amount of adsorption of polysaccharide in the presence of these surfactants and with the conformation of the created adsorption layer. Cationic CTAB added to the system easily forms complexes with nonionic GG (adsorption of GG in the presence of CTAB is high) but the adsorption of such a complex on the surface of manganese dioxide causes that the created adsorption layer is compact and thin because of the electrostatic attraction between CTAB and MnO<sub>2</sub> which is confirmed by small values of the adsorption layer thickness in the MnO<sub>2</sub>/0.1 M NaCl/100 ppm GG/0.0001 M CTAB system (Table 4). For of the above mentioned reasons, CTAB

is worse than TX-100 or SDS for the improvement of MnO<sub>2</sub> stability. In the case of nonionic TX-100 the influence of this surface active agent on the GG adsorption is rather small but the formed adsorption layer is more expanded towards the liquid phase (high values of the adsorption layer thickness) (Table 4). Under such conditions the MnO<sub>2</sub>/100 ppm GG system is more stable. However, as mentioned earlier, the anionic surfactant provides the highest stability of the suspension. In this case the adsorption of GG is almost as high as in the presence of CTAB but because of electrostatic repulsion between the negatively charged surfactant and the surface of MnO<sub>2</sub>, the thickness of the adsorption layer is high. Such a conformation of the adsorption layer expanded and containing a lot of polymer ensures the best stability of the system.

Taking into account the influence of the surfactant mixtures on the stability of MnO<sub>2</sub>/100 ppm GG suspensions one might notice that the addition of the surface active agents mixture to the suspension causes the increase of stability not only compared to the system with 100 ppm of GG but also to those containing single surfactants. The TSI values equal 12.84 and 2.89 for the CTAB/TX-100 and SDS/TX-100 systems respectively. The transmission in the case of the system with the mixture of cationic and nonionic surfactant reaches 30 % whereas in the latter system only 6 %. The explanation of this fact is connected with the synergistic effect of the surfactant mixtures on the adsorption of guar gum. It is known that the synergetic effect involves the increase of adsorptive, foaming and rewetting properties of surfactant mixtures in comparison to pure surfactant solutions (Wang and Kwak 1999; Reif and Somasundaran 1999; Soriyan et al. 2009). As mentioned earlier, the interactions between TX-100 and GG are small, but the presence of another ionic surfactant causes the increase of these interactions. The reason for that is the fact that the electrostatic interactions of ionic surfactants provide a sufficient number of hydrophobic sites for adsorption of nonionic surfactant (Somasundaran and Huang 1997). The obtained results are in agreement with the findings of Palla and Shah (2002) who noticed that mixtures of ionic and non-ionic surfactants are capable of stabilizing suspensions whereas the same surfactants added singly to the suspensions are not so effective. Among two studied surfactant mixtures better improvement of stabilization was

obtained in the presence of SDS/TX-100 mixture. Adsorption of guar gum in the presence of this mixture and the thickness of the created adsorption layer are the highest among all measured systems (Table 4). As a result, stability of the measured suspension is the highest too. In the case of CTAB/TX-100 the synergistic effect is visible but stability of the  $\text{MnO}_2$  suspension is lower in comparison to the previously discussed system. The reason for that is lower adsorption of guar gum in the presence of the CTAB/TX-100 mixture and electrostatic attraction between the polymer-surfactant complex and the surface of the adsorbent which causes that the adsorption layer is thinner.

## Conclusions

The addition of guar gum (in the concentration range 10–200 ppm) to the  $\text{MnO}_2$  suspensions increases their stability. The highest increase is observed in the presence of 200 ppm of GG. The reason for that is high adsorption and good coverage of metal oxide particles by polymer. However, the mixtures of guar gum and surfactants (CTAB, TX-100, SDS) are even better in stabilizing the above-mentioned suspension. Explanation of this phenomenon might be found in the increase of guar gum adsorption in the presence of surfactants, which results from multilayer complex formation. Among the single surfactants, the most effective one was SDS. It was the best in improving stability of the  $\text{MnO}_2/100$  ppm GG suspension. The adsorption of guar gum in the presence of this anionic surface active agent is high and the obtained adsorption layer is thick, which provides good stability. The most stable suspensions of  $\text{MnO}_2/100$  ppm GG are obtained in the presence of surfactant mixtures. The reason for that is the synergetic effect between the mixtures of cationic- nonionic surfactants as well as between the anionic and nonionic ones.

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