

Influence of surfactants on the adsorption and electrokinetic properties of the system: guar gum/manganese dioxide

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Abstract The adsorption of non-ionic polysaccharide—guar gum (GG) in the presence or absence of the surfactants: anionic SDS, cationic CTAB, nonionic TX-100 and their equimolar mixtures SDS/TX-100, CTAB/TX-100 from the electrolyte solutions (NaCl, CaCl₂) on the manganese dioxide surface (MnO₂) was studied. The increase of GG adsorption amount in the presence of surfactants was observed in every measured system. This increase results from formation of complexes between the GG and the surfactant molecules. This observation was confirmed by the determination of the influence of GG on surfactants adsorption on the MnO₂ surface. The increase of GG adsorption on MnO₂ was the largest in the presence of the surfactant mixtures (CTAB/TX-100; SDS/TX-100) which is the evidence of the synergetic effect. The smallest amounts of adsorption were obtained in the presence of TX-100, which results from non-ionic character of this surface active agent. In the case of single surfactant solution CTAB has the best efficiency in increasing the amount of GG adsorption on MnO₂ which results from strong interactions with GG and also with the negatively charged surface of the adsorbent. In order to determine the

electrokinetic properties of the system, the surface charge density of MnO₂ and the zeta potential measurements were performed in the presence of the GG macromolecules and the above mentioned surfactants and their mixtures. The obtained data showed that the adsorption of GG or GG/surfactants complexes on the manganese dioxide surface strongly influences the diffused part of the electrical double layer (EDL)—MnO₂/electrolyte solution, but has no influence on the compact part of the electric double layer. This is the evidence that the polymers chains are directly bonded with the surface of the solid and the surfactants molecules are present in the upper part of the EDL.

Keywords Polymer adsorption · Surfactant adsorption · Guar gum · SDS · CTAB · TX-100 · Manganese dioxide

Introduction

Guar gum (GG) is a natural, nonionic, non-toxic and biodegradable polysaccharide. This substance is produced from the seeds of the two annual leguminous plants, *Cyamopsis tetragonalobus* and *C. psoraloides* (Ma and Pawlik 2007). The functional polysaccharide in guar gum is guaran. It contains the units of β -D-mannopyranose with α -D-galactopyranose ones linked

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with the position (1 → 4) and connected to the mannose backbone through (1 → 6) glycosidic linkages. The polymannose is randomly substituted with galactose. The degree of substitution of polymannose varies from 1.8 to 1.0 (Ma and Pawlik 2005). Because of the random nature of this substitution, the least substituted sections of the guar gum show the greatest tendency to associate, while the more densely substituted regions serve to solubilize the polymer chains (Ma and Pawlik 2007). The chemical structure of this compound is shown in Table 1. As one can see each unit contains nine hydroxyl groups. These groups are available for hydrogen bonding of the guar gum macromolecules to the mineral surfaces. The average molecular weight of guar gum ranges from 1 to 2 million (Cheng et al. 2002). Guar gum is widely used in many branches of industry such as pharmaceuticals, cosmetics, textiles, food and mineral industries (Wang et al. 2005). It is commonly used as a depressant for hydrophobic gangue minerals in the flotation of nickel and platinum bearing ores (Wang et al. 2005) or as a blinder of water-insoluble slimes in potash flotation (Ma and Pawlik 2005). Despite many efforts, the mechanism of interaction between polysaccharides and solids is not well understood, which limits wider application of these substances. It has been reported that polysaccharides can adsorb on mineral surfaces through complexation with metal–hydroxyl surface sites (Liu and Laskowski 1989a, b). The nature of the interaction is of acid–base type and strongly depends on the acidity of the surface metal–hydroxyl groups (Liu et al. 2000). However, other mechanisms such as hydrogen bonding, hydrophobic interactions, electrostatic attraction have been also taken into account (Pugh 1989; Morris et al. 2002).

As far as adsorption of guar gum is concerned, hydrophobic interactions were proposed for guar gum adsorption onto talc by Steenberg and Harris (1984) as well as Jenkins and Ralston (1998). However, Rath and Surbamanian (1997), Jucker et al. (1997) as well as Ma and Pawlik (2005, 2007) suggested that hydrogen bonding and chemical interactions between macromolecules of guar gum and the surface of the adsorbent are the main driving force in this process. This was confirmed by Wang et al. (2005) who observed the decrease in guar gum adsorption onto the talc surface in the presence of urea, which is a hydrogen bond breaker. Due to the fact that the adsorption of guar gum is not affected by ionic

strength, the authors also concluded that hydrogen bonding is responsible for guar gum adsorption onto talc. Very interesting conclusion was drawn by Bicak et al. (2007). They found out that at low pH values the dominant mechanism of guar gum adsorption on pyrite is hydrogen bonding, but with the alkaline pH values the mechanism that can be postulated is acid–base reaction with the effect of iron oxy/hydroxyl ions present at pH 9 and 11.

Research on the adsorption of GG on the mineral surface usually concerning the influence of pH, ionic strength and GG molecular weight is the most frequent (Steenberg and Harris 1984; Jenkins and Ralston 1998; Rath and Surbamanian 1997; Jucker et al. 1997; Wang et al. 2005; Bicak et al. 2007). However, the influence of surfactants on the adsorption and the electrokinetic properties of the system polysaccharide–metal oxide system is neglected. Because of that the aim of this paper was to analyse the influence of the surfactants: anionic SDS, cationic CTAB and non-ionic TX-100 and their mixtures with the molecular ratio 1:1 on the adsorption of GG on the MnO₂ surface as well as to analyse the electrokinetic properties (surface charge density, zeta potential) of the guar gum/manganese dioxide system in the presence of surfactants. Measurements were made in 0.01 mol dm⁻³ NaCl and in 0.003 mol dm⁻³ CaCl₂ which gave the opportunity to compare the impact of background electrolyte on the analysed systems.

From the literature reports it is well known that polymers can interact with the surface active agents (Moudgil and Prakash 1998; Parida et al. 2006; Nylander et al. 2006). The interactions responsible for the adsorption process of polymer macromolecules in the presence of surfactants might be as follows: electrostatic attraction, covalent bonding, hydrogen bonding and non-polar interactions. The interest in this type of interactions results from the fact that the mixtures of polymers and surfactants are widely used in many branches of industry (Somasundaran and Krishnakumar 1997). One of the significant feature of surfactants is their ability to lower the interfacial tension between an aqueous solution and other phase. In the absence of the polymer the surfactant molecules, at concentrations beyond a critical micelle concentration, aggregate in aqueous solutions and form spherical, globular, rodlike micelles or spherical bilayer vesicles (Nagarajan 2001). The type of aggregate structure depends on the nature of the surfactant head

Table 1 Names and structures of organic chemical compounds used in the measurements

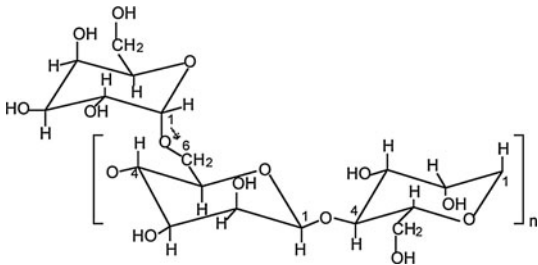
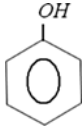
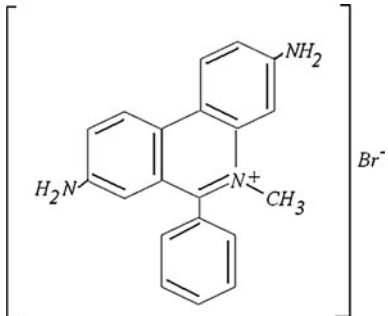
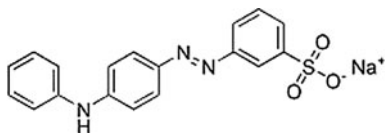
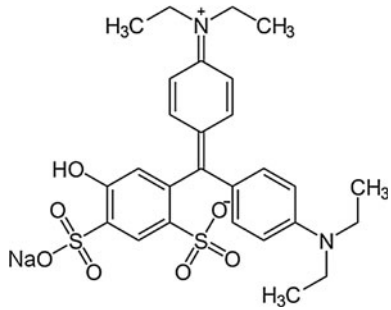
Name	Chemical name	Chemical structure
GG	Guar gum	
SDS	Sodium dodecylsulfate	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_2^- \text{Na}^+$
CTAB	Hexadecyltrimethylammonium bromide	$\left[\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3 \right] \text{Br}^-$
TX-100 (Triton X-100)	T-octylphenoxypoly-ethoxyethanol	$\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_n\text{OH}$ <p style="text-align: right;"><i>n</i>~9.5</p>
Phenol	Hydroxybenzene	
Chloroform	Trichloromethane	CHCl_3
Dimidium bromide	3,8-Diamino-5-methyl-6-phenylphenanthridinium bromide	
Metanil yellow	Methylum, tris(4-(dimethylamino)phenyl)-, salt with 3-((4-(phenylamino)phenyl)azo)benzenesulfonic acid (1:1)	

Table 1 continued

Name	Chemical name	Chemical structure
Patent blue	[4-(alpha-(4-diethylaminophenyl)-5-hydroxy-2,4-disulfophenyl-methylidene)2,5-cyclohexadien-1-ylidene] diethylammonium hydroxide, sodium salt	
Acetic acid	Ethanoic acid	CH ₃ COOH
Sodium acetate	Sodium ethanoate	CH ₃ COONa

group (ionic, nonionic, zwitterionic) and the tail group (hydrocarbon or fluorocarbon, branching, unsaturation, aromaticity). However, the addition of polymer to the surfactant solution causes the early aggregation of surface active compounds at the concentration lower than the critical micelle concentration (cmc). This lower concentration is called the critical aggregation concentration (cac) (Jönsson et al. 1998). Under such concentration starts the formation of small assemblies, but at concentrations higher than cmc binding of assemblies with the polymers is completed. Then the surfactants start to form normal micelles. This point is known as the extended cmc or cmc_e (Mitra et al. 2008). Between cac and cmc_e polymers and surfactants may form a new phase called the “coacervate” (Wang et al. 2000) which can grow into large assemblies by self-association. Eight main types of polymer–surfactant interactions can be distinguished depending on the molecular structures of the polymer and the surfactant and on the nature of the interaction forces (Nagarajan 2001). One—polymer and the surfactant are oppositely charged. The main force responsible for the association is electrostatic attraction. Created complex has a reduced charge and reduced hydrophilicity. These complexes may precipitate from the solution. Two—surfactant and polymer are also opposite charged but the surfactant promotes intramolecular interactions with polymer chains either interacting with multiple sites on one molecule or intermolecular bridging by interacting simultaneously with sites on different polymer chains. Three—the polymer is un

uncharged random or multiblock copolymer. The surfactant molecules orient themselves at domain boundaries separating the polymer segments of different polarities. Four—polymer is hydrophobically modified and individual surfactants molecules associate with one or more of hydrophobic modifiers on a single polymer chain or multiple polymer molecules. However, interaction between surfactant does not change the conformation of polymer. Five and six—polymer is also hydrophobically modified but surfactant form co-aggregates with multiple hydrophobic modifiers belonging to the same polymer molecule, causing the polymer conformation to change (five) or at larger surfactant concentrations, surfactant aggregates are formed around each of the hydrophobic modifier (six). Seven—the polymer segments partially penetrate and wrap around the polar head group region of the surfactant micelles reducing the micelle core-water contact. A single polymer molecule can associate with one or more surfactant micelles. Eight—polymer molecule does not interact with surfactants for electrostatic or steric reasons.

Maltesh and Somasundaran found out that polyethylene oxide (PEO) which normally does not adsorb on the alumina surface, in the presence of sodium dodecylsulphate (SDS) is inducted into the adsorption by preadsorbed SDS, which is typical reaction of complex formation (Maltesh and Somasundaran 1992). Ghodbane and Donoyel (1997) studied competitive adsorption on silica between non-ionic surfactants of the alkyl phenolpoly(ethylene oxide) type

(TX-100) and neutral polymers of the poly(ethylene oxide) type (PEG). They found out that for molecular weights of the polymer below 10,000 g/mol surfactant adsorption was not affected by the presence of the polymer. For higher molecular weights, polymer macromolecules are preferentially adsorbed at low concentrations, whereas at higher concentrations the behaviour of these systems can be characterized by a threshold molecular-weight value, above which the polymer displaced the surfactant. According to Yamana and Esumi (1997) who investigated the interactions of the non-ionic water soluble polymers: hydroethylcellulose (HEC) and hydroponically modified HEC (HMHEC) with the anionic surfactant (SDS) on the surface of alumina and graphite for the HEC-SDS-alumina and HMHEC-SDS-alumina systems, the adsorption of polymer is enhanced by the addition of SDS, owing to the formation of polymer-surfactant complexes at the alumina-solution interface.

Sodium dodecyl sulphate (SDS) ($C_{12}H_{25}SO_4Na$) was used as an anionic surfactant. Its molecule has a tail containing 12 carbon atoms and the sulphate group which gives the amphiphilic properties required from a detergent. SDS has a wide range of applications 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 providing a buffer solution for the extraction of DNA, synthesis of nanoparticles and hair conditioning products (Pan et al. 2006; Chakraborty et al. 2006).

T-octylphenoxypolyethoxyethanol known as TX-100 or Triton X-100 (the trade name), ($C_8H_{17}C_6H_4(OCH_2CH_2)_n \times OH$; $n \sim 9.5$) was used as a nonanionic surfactant in the presented measurements. This compound has also a wide range of applications. It is frequently used in stabilization of biochemistry processes (Preté et al. 2002).

Manganese dioxide was chosen as an adsorbent. This chemical compound is one of the most stable manganese (IV) compounds. It occurs in nature as a mineral pyrolusite. Manganese dioxide forms a few polymorphic modifications (α , β , γ). MnO_2 is insoluble in water. 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). What is more, its chemical

inertness, stability in a broad pH range and well-defined interface allow to use this chemical compound as an adsorbent in many adsorption processes.

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 μm , with a volume average size of 6.78 μm . 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. The average molecular weight of guar gum was found to be 1.5×10^6 . It was estimated using a goniometer with a laser light scattering system BI 200SM (Brookhaven Instruments). The example formula of guar gum is presented in Table 1.

SDS, CTAB and TX-100 (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 the exceeding of the critical micelle concentration. For SDS the critical micelle concentration is $0.00825 \text{ mol dm}^{-3}$ (Rodríguez-Cruz et al. 2005), for CTAB 0.00086 (Xi and Guo 2007) whereas for TX-100— $0.00029 \text{ mol dm}^{-3}$ (Rharbi and Winnik 2001). Both NaCl and $CaCl_2$ produced by Fluka were used as the supporting electrolytes.

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 amount of polymer adsorption, elektrokinetic properties of the measured system as well as stability of the obtained suspensions (Wiśniewska 2010, 2011, 2012).

Methods

Adsorption measurements

10 mL of the solution was prepared from the polymer stock solution (GG), electrolyte (NaCl or CaCl₂), doubly-distilled water and surfactant (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. Next pH was adjusted to the desired value using 0.1 mol dm⁻³ HCl and 0.1 mol dm⁻³ NaOH. Seven different initial concentrations of GG were used (25–300 ppm). 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 calorimetric 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). Time of centrifugation equalled 15 min. After 30 min of colour development the absorbance was measured at a wavelength of 490 nm using a spectrophotometer (Cary 100, Varian). All measurements were made as triplicates. In this paper the average values are reported. The amount of GG adsorption on the MnO₂ surface was calculated from a calibration curve according to the concentration difference before and after the adsorption tests.

The concentration of SDS was analysed by a variation of the method from Zerbe et al. (2000) (Zeng et al. 2004). 1 L indicator solution was prepared by dissolving 0.16 g dimidium bromide, 0.04 g patent blue and 40 mL of 1.25 M sulphuric acid in doubly-distilled water. Then 0.5 mL of sample solution was mixed with 39.5 mL doubly-distilled water; followed by the addition of 10 mL solution of indicator and 20 mL of chloroform. The mixture was shaken for 1 min and allowed to phase-separate. Then a few millilitres of chloroform phase were taken for further analysis. The SDS concentration was measured spectrophotometrically at 526 nm, using pure chloroform as the reference. The SDS concentration in the samples was calculated from a calibration curve.

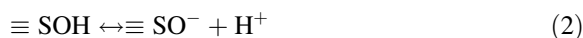
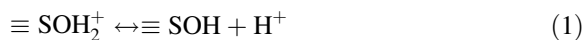
The concentration of CTAB was determined with a method similar to that used for SDS (Whitby et al. 2001). A CTAB-containing sample (0.5 mL) was

mixed with distilled water (15 mL), a buffer solution composed of equimolar (1 M) concentrations of acetic acid and sodium acetate (5 mL), 10⁻³ M metanil yellow solution (5 mL), and chloroform (10 mL) in a separation funnel. The separation funnel was shaken for 1 min, and then the mixture was allowed to stand for 1 h. The CTAB concentration was obtained by analyzing the organic phase spectrophotometrically at 404 nm, using pure chloroform as the reference. The CTAB concentration in the samples was calculated from a calibration curve.

The concentration of TX-100 was also analysed spectrophotometrically directly from UV absorbance at a wavelength 278 nm with pure water as the reference (Zeng and Osseo-Asare 2004). The TX-100 concentration in the samples was calculated from a calibration curve.

Potentiometric titration

The 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 electric double layer, background electrolyte ions are assumed to adsorb non-specifically, but in modern models these ions undergo also the specific adsorption.

Comparison of the titration curve of and that of the metal oxide suspension 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:

$$\sigma_0 = \frac{\Delta V c F}{m S} \quad (3)$$

where ΔV —dependence between the volume of acid/base added to the suspension in order to obtain the desired pH value, c —molar concentration of acid/base, F —Faraday constant ($9.648 \times 10^4 \text{ C mol}^{-1}$),

m —mass of metal oxide, S —specific surface area of metal oxide.

MnO_2 surface charge density in the presence and absence of GG and surfactant (SDS, CTAB, TX-100 and their mixtures with the molecular ratio 1:1) was determined using the potentiometric titration method. The NaCl concentration was 0.01 mol dm^{-3} whereas CaCl_2 concentration equalled $0.003 \text{ mol dm}^{-3}$. Such concentrations of the salts provided the required ionic strength of the solutions ($I = 0.01$) for both electrolytes. 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 MnO_2 surface charge was determined using the “Miar_t” programme written by W. Janusz. The volume of the measured solution was 50 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 5 %.

Zeta potential measurements

0.05 g of manganese dioxide was added to 500 cm^3 of the supporting electrolyte solution (NaCl or CaCl_2) with or without GG and surfactants (SDS, CTAB, TX-100 and their mixtures with the molecular ratio 1:1). 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 (ζ) was calculated from the Smoluchowski equation (Lyklema 2003). The zeta potential measurements were made as triplicates and the results were obtained with the measurement uncertainty from 2 to 6 %. In the paper the average values are reported.

Thickness of adsorption layer

The thickness of the polysaccharide adsorption layer (δ) 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 (δ). It results in the increase of volume fraction (ϕ_0) of the dispersed solid. Thus the values δ were obtained from the dependency:

$$\delta = r \left[\left(\frac{\phi_p}{\phi_0} \right)^{1/3} - 1 \right] \quad (4)$$

where r —the radius of the metal oxide particle, ϕ_p —the volumetric fraction in the presence of polymer, ϕ_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:

$$\frac{\eta}{\eta_0} = 1 + k\phi_0 \quad (5)$$

where η is viscosity of the suspension (Pa s), η_0 is viscosity of the liquid phase (Pa s), and k is Einstein coefficient. The coefficient k is equal to 2.5 for the rigid spherical particles in infinitely diluted suspensions.

The volumetric fraction (ϕ_p) in the presence of polymer or polymer-surfactant complex was determined from linear dependency of η/η_0 versus ϕ_0 of manganese dioxide (calibration curve). The viscosity measurements enabling the η/η_0 ratio determination in the presence of polymer polymer-surfactant complex were made with the volume fraction of MnO_2 equal to 13.7×10^{-3} . Because the adsorption of polymer or polymer surfactant complex caused the increase of the ratio value ϕ_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. 4).

Results and discussion

Figures 1, 2 illustrate the adsorption kinetics of guar gum on the MnO_2 surface in the presence of 0.01 mol dm^{-3} NaCl (Fig. 1) and $0.003 \text{ mol dm}^{-3}$ CaCl_2 (Fig. 2). These measurements were performed in order to estimate the time needed to achieve the adsorption–desorption equilibrium before the measurements of the adsorption amount of the polymer. As one can see from the presented data the adsorption equilibrium in the presence of pure electrolyte solutions and in the absence of the surface active agents is reached almost immediately. The time needed to achieve the adsorption–desorption equilibrium equalled less than 60 min in both electrolytes. The situation

was a bit different in the presence of surfactants and their mixtures. The equilibrium time is reached in a very wide range from 100 min (in the presence of TX-100 in 0.01 mol dm⁻³ NaCl) to 1,100 min (in the presence of CTAB, CTAB/TX-100 and SDS/TX-100 in the presence of 0.003 mol dm⁻³ CaCl₂). The reasons for longer time needed to achieve the adsorption equilibrium are the reconformations in the measured systems. They result from the interactions between the electrolyte cations, guar gum macromolecules and the surfactant molecules along with the interactions with the surface of the solid. Of course, the possibility of reconformations is also in the systems with pure electrolyte solutions but one should bear in mind that it is higher in the presence of surfactants and divalent cations. Considering the results of the kinetic measurements 1,100 min (18 h) was chosen to be the conditioning time in all adsorption measurements. This time could be shorter for the systems where there were no surfactants but the

author decided to provide the identical parameters of the adsorption processes in all measured systems.

The Langmuir adsorption isotherms of guar gum on the MnO₂ surface (c/Γ vs. c) at 25 °C in the presence or absence of surfactants (SDS, CTAB, TX-100 and their mixtures: SDS/TX-100 and CTAB/TX-100 with the molar ratios 1:1) are presented in Figs. 3 and 4. Measurements were performed at pH \cong 6 and in the presence of two different background electrolytes: 0.01 M NaCl (Fig. 3) and 0.003 M CaCl₂ (Fig. 4). The experimental data of the GG adsorption on the MnO₂ were fitted to the Langmuir adsorption isotherm model according to the equation:

$$\frac{c}{\Gamma} = \frac{1}{K(\Gamma)_{\max}} + \frac{c}{(\Gamma)_{\max}} \quad (6)$$

where c is equilibrium concentration of polymer in the solution (mol/dm³), Γ is adsorbed amount of polymer on the solid surface (mol/m²), $(\Gamma)_{\max}$ is maximum adsorbed amount corresponding with the totally filled

Fig. 1 Kinetics of guar gum adsorption (100 ppm) on the MnO₂ surface in the presence and absence of surfactants, 0.01 M NaCl, pH = 6

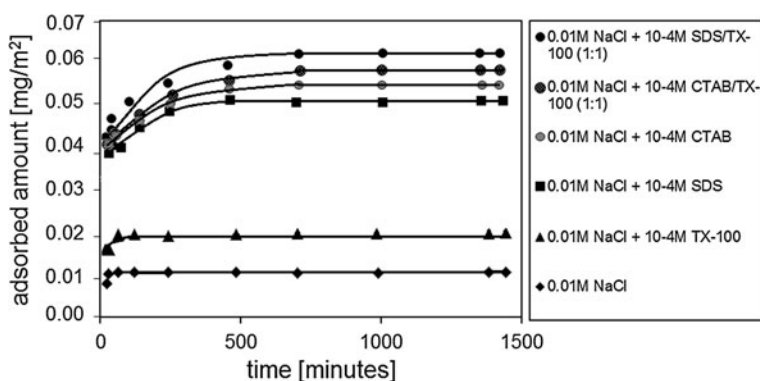


Fig. 2 Kinetics of guar gum adsorption (100 ppm) on the MnO₂ surface in the presence and absence of surfactants, 0.003 M CaCl₂, pH = 6

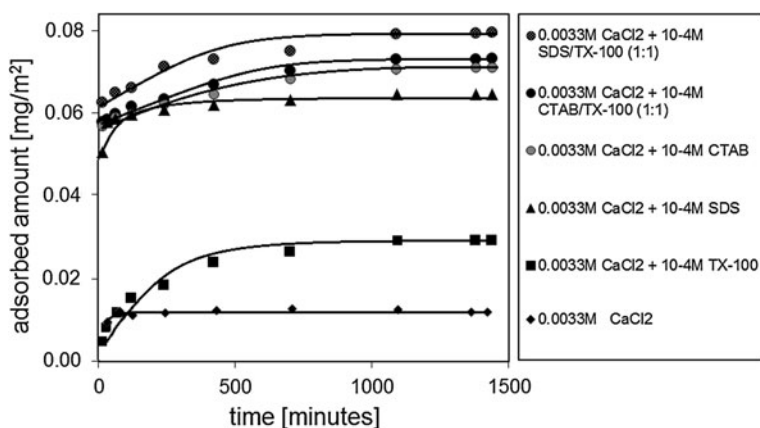


Fig. 3 Langmuir adsorption isotherms of guar gum on MnO_2 in the presence and absence of surfactants, in 0.01 M NaCl solution, pH = 6

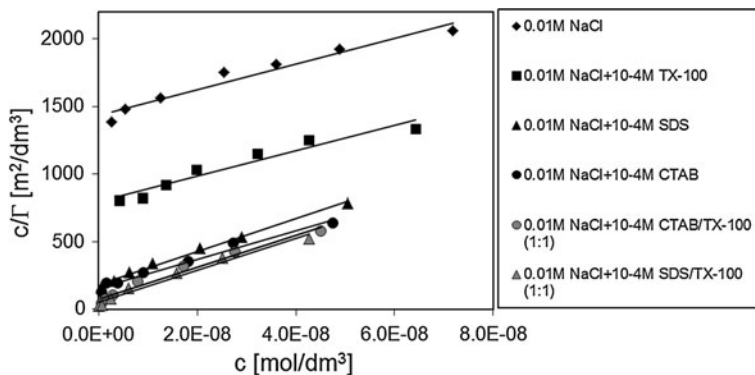
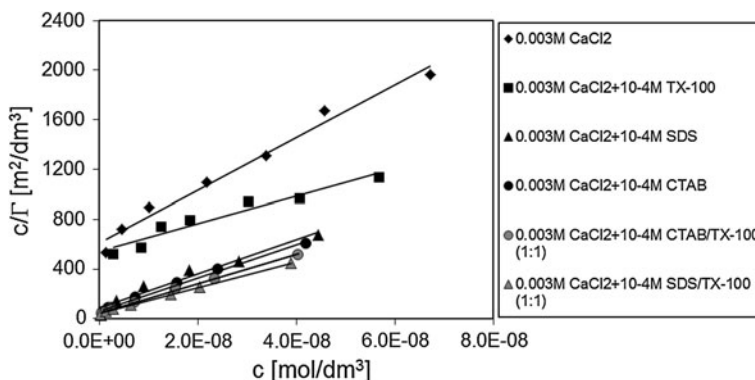


Fig. 4 Langmuir adsorption isotherms of guar gum on MnO_2 in the presence and absence of surfactants, in 0.003 M CaCl_2 solution, pH = 6



monolayer (mol/m^2). The values of K and $(\Gamma)_{\text{max}}$ were determined from the intercept and the gradient of these plots, respectively.

The free energies of adsorption (ΔG_{ads}) were calculated from the equation:

$$\Delta G_{\text{ads}} = -RT \ln K \quad (7)$$

where R is gas constant ($8.314 \text{ J}/(\text{K} \times \text{mol})$) and T is temperature (298 K).

Figures 3 and 4 present the Langmuir adsorption isotherms of guar gum on the MnO_2 surface in the absence and presence of surfactants (SDS, CTAB, TX-100 and their mixtures SDS/TX-100 and CTAB/TX-100 with the molar ratio 1:1). Measurements were made in the presence of NaCl as the background electrolyte (Fig. 3) as well as in the presence of CaCl_2 (Fig. 4). Concentrations of these electrolytes were chosen to obtain the same values of ionic strength. Mechanism of polysaccharides adsorption on the solid surface results from hydrophobic and (or) electrostatic interactions. Hydrogen bonding and hydrophobic interaction seem to be the most “popular” adsorption mechanisms (Morris et al. 2002; Steenberg and

Harris 1984). However, according to other scientists (Liu and Laskowski 1989a, b) the adsorption of polysaccharides results from the acid–base reaction between the polymer macromolecules and the metal hydroxyl groups from the solid surface. From the zeta potential data (Fig. 7) it is clearly visible that in the presence of 0.01 mol dm^{-3} NaCl the isoelectric point of manganese dioxide is located around pH 4–5. Below this pH value the MnO_2 surface is positively charged and above it is negative. At pH 6 the surface of manganese dioxide is negatively charged because of a large number of MnO^- , but the number of hydroxyl groups is also very large. Because a macromolecule of guar gum contains a lot of hydroxyl groups the dominant mechanism of GG adsorption on the MnO_2 surface under such conditions can be postulated as hydrogen bonding or/and hydrophobic interactions. However, the adsorption mechanism becomes much more complicated when the surface active agent is added to the measured system. As one can see from Figs. 3 and 4 the adsorption of guar gum increases in the presence of surfactants and their mixtures. This increase is the smallest in the presence of non-ionic

TX-100, larger in the presence of anionic SDS and cationic CTAB and the largest when the surfactant mixtures CTAB/Triton-100 or SDS/TX-100 are added to the adsorption system. As for these two mixtures a larger increase in the amount of GG adsorption on MnO_2 is observed when the SDS/TX-100 mixture was used. The increase of guar gum adsorption in the presence of surfactants may result from formation of complexes between a few chains of guar gum and at least one (or more) molecule of a surfactant. The strong evidence for complex formation between the guar gum macromolecules and surfactant molecules is presented in Table 2. It presents the thickness of guar gum adsorption layer in the presence of different surfactants. As one can see, the large differences between the thickness of polymer adsorption layers in the absence and in the presence of surfactants point out that there is more than one macromolecule of polymer adsorbed on one active centers. Unfortunately, the nature of complexes between polysaccharides and surfactants has not been fully understood. They are definitely non-electrostatic because of non-ionic character of used polysaccharide. Possible mechanisms are hydrophobic interactions between the GG and the surface active molecules as well as hydrogen bond ones. As one can see from Figs. 3 and 4 the amount of GG adsorption is the smallest in the presence of TX-100, which means that the GG-TX-100 complexes are created less effectively than in the case of other surfactants. The interactions between the non-ionic surfactants and the neutral polymers is reported in the literature (Winnik 1990) but it is rather weak and occurs as the effect of the tendency towards the reduction in the free energy of the total system (Winnik and Regismond 1996). They occur between the surfactants and sufficiently hydrophobic polymers and the association between these two substances takes place at the surfactant concentrations lower than cmc (Winnik and Regismond 1996). The addition of the ionic surfactants SDS or CTAB increases the adsorption amount of guar gum more significantly, which is a consequence of stronger interactions between the ionic surfactants and the uncharged polymers (Nagarajan 2001). The exact nature of these interactions is still far from being well understood especially in the case of the nature of attraction forces. It is known that the interactions between the ionic surfactants and the neutral polymers start at the cac below the cmc (Van Stam et al. 1995).

As far as the influence of SDS on the GG adsorption is concerned, from Figs. 3 and 4 it can be clearly seen that the presence of an anionic surfactant causes a larger increase in GG adsorption amount on the MnO_2 surface than the presence of TX-100 but lower than CTAB. What is interesting and surprising, the literature reports concerning the interactions between SDS and gums are contradictory. Nedjhiouia et al. (2005) proved strong interactions between SDS molecules and xanthan gum using conductivity and surface tension measurements, whereas the measurements made by Mukherjee et al. (2010) showed that SDS has no influence on GG, Triton X-100 produced moderate interactions and CTAB strongly interacts with guar gum. However, one should bear in mind that the above mentioned results concern only the interactions between SDS and GG in pure solutions not on the surface of the solid. Because of the presence of another component in the adsorption system these interactions might be different. The reason for that is that the metal oxide which can interact with surfactants, polymer as well as with polymer-surfactants complexes. According to the results presented here SDS influences the GG adsorption amount larger than that of TX-100 but smaller than that of CTAB. The interaction between ionic surfactants and GG might be the hydrogen bond type or/and hydrophobic. In the case of the mechanism of anionic surfactants and GG interactions the association between the hydroxyl groups of GG with the surfactant head group exists. In the case of cationic CTAB strong interaction with guar gum was confirmed using the tensiometry, conductometry, isothermal titration calorimetry, viscometry and AFM techniques (Mukherjee et al. 2010). Moreover, the analysis of the results shown in Figs. 3 and 4 allows to conclude that the presence of surfactant SDS/TX-100 and CTAB/TX-100 mixtures causes the largest increase of the adsorption amount of GG. The reason for that is the fact that the mixtures of ionic and non-ionic surfactants exhibit synergetic effect (Wang and Kwak 1999; Reif and Somasundaran 1999; Soriyan et al. 2009) resulting in the increase of adsorptive, foaming and rewetting properties of surfactant mixtures in comparison to pure surfactant solutions. As was said above the interactions between non-ionic surfactant and GG are small, but the presence of another surfactant, the ionic one causes the increase of these interactions. It was proposed that the electrostatic interactions of ionic surfactants provides a

Table 2 The thickness of guar gum adsorption layer in the presence of different surfactants

System	Thickness of polymer adsorption layer (nm)
GG/MnO ₂	6.7
GG/MnO ₂ /TX-100	13.6
GG/MnO ₂ /SDS	15.9
GG/MnO ₂ /CTAB	11.4

Concentration of guar gum 100 ppm, concentration of surfactants 10^{-4} mol dm⁻³, background electrolyte 10^{-2} mol dm⁻³ NaCl, pH = 6

sufficient number of hydrophobic sites for adsorption of nonionic surfactant (Somasundaran and Huang 1997). Comparing two studied surfactant mixtures a bit larger adsorption amount of GG was obtained in the case of the SDS/TX-100 mixture than the CTAB/TX-100 one but the difference was small.

Comparison of the data presented in Figs. 3 and 4 let us draw conclusions concerning the influence of electrolyte on the GG adsorption on MnO₂ surface. As one can see the amounts of GG adsorption in the presence of CaCl₂ are a bit higher when calcium chloride is used as a background electrolyte. Divalent calcium cations may definitely be adsorbed on the negative MnO₂ surface but they also might interact with the guar gum macromolecules. The consequence of that is the increase of GG adsorption amount in the presence of this electrolyte. What is more the free energies of hydration are larger for Ca²⁺ ions than Na⁺ (Tissandier et al. 1998). Calcium ions are smaller and more strongly hydrated than sodium. Because of that calcium ions can be treated as kosmotropes, whereas sodium as chaotropes (Ma and Pawlik 2006). Kosmotropes have the ability to increase the stability of intermolecular forces in the hydrogen bonding interactions and van der Waals forces, whereas chaotropes disrupt the structure of macromolecules and increase the entropy of the system by interfering with intramolecular interactions such as hydrogen bonds, van der Waals forces, and hydrophobic effects. Because of that the adsorption of GG in the presence of CaCl₂ might be a bit larger than in the presence of NaCl.

Another evidence that the complexes between the guar gum chains and the surface active agent molecules are created is presented in Figs. 5 and 6. Figures 5 and 6 present the influence of 100 ppm of

guar gum on the surfactants (CTAB, SDS, Trion X-100) adsorption on the MnO₂ surface in the presence of 0.01 M NaCl (Fig. 5) and 0.003 M CaCl₂ (Fig. 6). The first observation in the obtained data is that the surfactants adsorption amount is always larger when guar gum is added to the adsorption systems. It definitely results from formation of complexes between at least two guar gum macromolecules and surfactants. The surface active agent molecules may interact with the macromolecules of GG and then they adsorb as complexes. Secondly, as one can see for the three measured pure surfactant solutions the adsorption amount of CTAB is the largest, then that of TX-100 and the lowest adsorption is observed for SDS. This order is the same in both measured electrolytes and it results from both the chemical character of used surfactants and the charge of the metal oxide. Point of zero charge for MnO₂ is located between pH 4–4.5, so at pH = 6 the surface of the manganese dioxide is negatively charged because of a large number of MnO⁻ groups (see Figs. 7, 8). Because of strong attraction forces between the positively charged CTAB and the negative surface the adsorption amount of this surfactant is the largest. On the other hand, the electrostatic repulsion between anionic SDS and the negatively charged MnO₂ is the reason for very low adsorption of this surface active agent. The amount of non-ionic TX-100 adsorption on MnO₂ is medium. In this case the mechanism of adsorption is non-electrostatic, probably hydrogen bond type, acid–base reaction or complex formation. A comparison between the amounts of pure surfactants adsorption in both measured electrolytes indicates that the amounts of TX-100 and SDS adsorption are larger in the presence of CaCl₂ which suggests complex formation between the calcium cations and the above mentioned surfactants. Ca²⁺ ions are strongly attracted by negative surface as well as complexes of calcium ion-TX-100 or calcium ion-SDS and this is why the adsorption of these two surfactants is larger in the presence of CaCl₂ than in NaCl. The situation is different in the case of CTAB. Here the amount of adsorption of CTAB is lower when CaCl₂ is used as a background electrolyte. Because both CTAB and Ca²⁺ ions are of the same charge they can compete for the same adsorption active centres and this is the reason for the decrease of CTAB adsorption in the presence of CaCl₂. The data presented in Figs. 5 and 6 allow also to draw an important conclusion about the influence of guar gum

on the adsorption of these three surfactants. As one can see, the addition of guar gum to the adsorption systems causes the increase of surfactants adsorption amount in every measured system. These results confirm formation of complexes between the guar gum and three measured surfactants. The amounts of surfactants adsorption in the presence of guar gum are the highest for CTAB, then for SDS and the lowest for TX-100. The obtained order is the same as that of guar gum adsorption in the presence of CTAB, SDS and TX-100. This is the evidence that the GG-CTAB-GG complexes are created and adsorbed more effectively than the GG-SDS-GG ones and also that the smallest possibility of complex formation is observed for non-ionic TX-100. Another conclusion that might be drawn from the presented data is that the influence of guar gum on the adsorption of surfactants is the largest in the case of SDS. The amount of adsorption of this surfactant increases drastically in the presence of guar gum. That might suggest strong interaction between these two substances. Nevertheless, despite the strong interaction between SDS and GG the adsorption of SDS-GG-SDS complexes on the negatively charged surface of MnO_2 is lower than that of CTAB-GG-CTAB complexes.

Figures 7 and 8 show the influence of pH as well as the presence of guar gum and the surfactants (TX-100, SDS, CTAB and their mixtures: SDS/TX-100; CTAB/TX-100 with the molar ratio 1:1) on the surface charge of MnO_2 . As it can be clearly seen in Figs. 7 and 8 the surface charge of MnO_2 depends on pH of the solution. At pH values lower than the point of zero charge for manganese dioxide ($\text{pH}_{\text{pzc}} < 4.5$), the solid surface is positively charged. Under such conditions the concentration of positively charged groups (MnOH_2^+) is the highest. At pH values higher than pH_{pzc} , the

surface of MnO_2 becomes negatively charged because of the increasing concentration of MnO^- groups. However, the presence of non-ionic guar gum or guar gum and all measured surfactants does not change the values of the surface charge of MnO_2 in the whole measured pH range. Because the presence of the guar gum macromolecules and the surfactants molecules does not change the values of the surface charge of MnO_2 , the shift of the point of zero charge is not observed. This fact results from the non-ionic character of used polysaccharide. The second important observation is that there is no significant difference between the surface charge density of MnO_2 in the presence of guar gum and different surfactants. This fact together with the results of the zeta potential measurements suggests that the surfactants molecules are not directly adsorbed on the surface of the solid in the presence of polymer (the surface charge of MnO_2 is the same in the presence of different surfactants) but they are bonded with the surface by the polysaccharide-surfactant complexes. The comparison of the data presented in Figs. 7 and 8 let us draw a conclusion about the influence of the background electrolyte on the surface charge density of MnO_2 . As one can see, in the presence of CaCl_2 the surface charge density of MnO_2 is different from the values obtained in the NaCl solution. The reasons for that are differences between the adsorption of calcium and sodium cations as well as chloride anions on the surface of the measured metal oxide.

Figures 9 and 10 present the influence of guar gum, surfactants (SDS, CTAB, TX-100) and their mixtures (SDS/TX-100, CTAB/TX-100) with the molar ratio 1:1 on the zeta potential of manganese dioxide. As it can be clearly seen from the obtained data, the presence of GG together with the surfactants might

Fig. 5 Influence of guar gum on the surfactants (CTAB, SDS, TX-100) adsorption on the MnO_2 surface in the presence of 0.01 NaCl , $\text{pH} = 6$

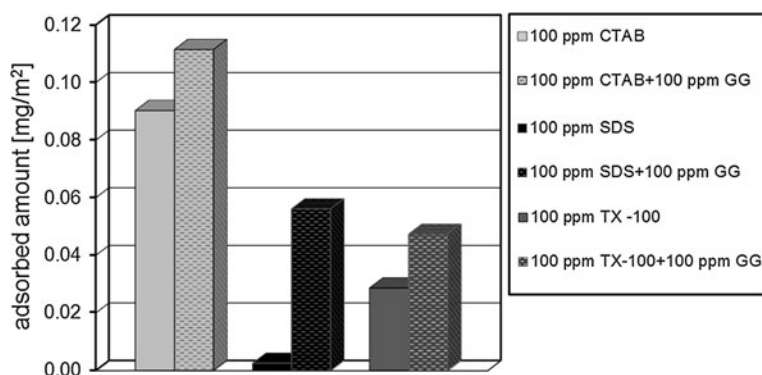


Fig. 6 Influence of guar gum on the surfactants (CTAB, SDS, TX-100) adsorption on the MnO_2 surface in the presence of 0.003 CaCl_2 , $\text{pH} = 6$

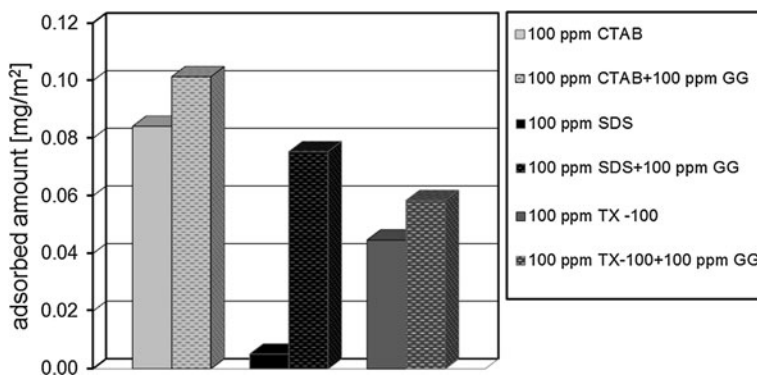


Fig. 7 Surface charge density of the system $\text{MnO}_2/0.01 \text{ M NaCl}$ in the absence and presence of guar gum (100 ppm) and surfactants

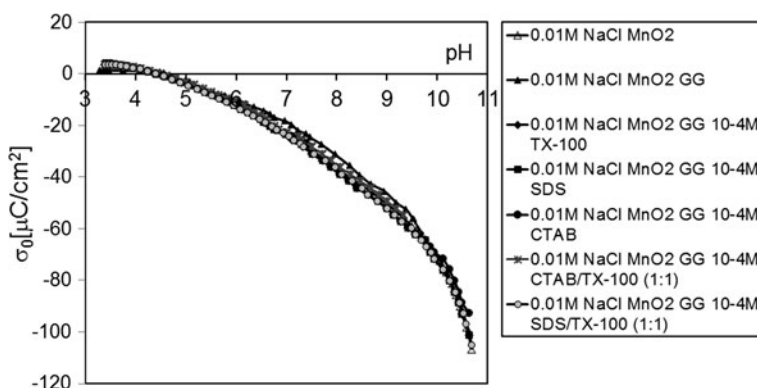
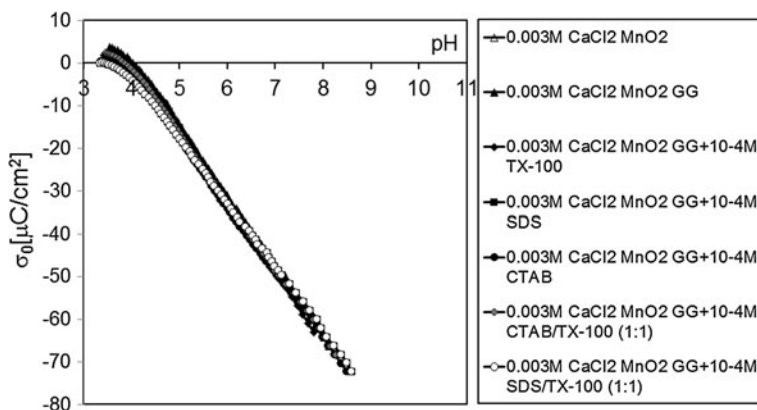


Fig. 8 Surface charge density of the system $\text{MnO}_2/0.003 \text{ M CaCl}_2$ in the absence and presence of guar gum (100 ppm) and surfactants



increase or decrease of the zeta potential of MnO_2 . Moreover, a shift of isoelectric point (pH_{iep}) of MnO_2 is also observed. The zeta potential values of MnO_2 are the highest in the presence of GG and CTAB and in the system where except for GG and CTAB TX-100 is also present. The reason for that is the chemical character of CTAB. Positively charged groups from this surfactant are present in the diffused part of the electrical double layer which causes the increase of the values of the MnO_2 zeta potential. It should also be mentioned that

in every system containing surfactant and polymer molecules the adsorption of polymer-surfactant complexes causes the shift of the slipping plane towards the bulk phase. This effect is responsible for the decrease of the zeta potential of MnO_2 but it seems to be smaller than the effect connected with the presence of the charge in the electrical double layer. This is why the increase of the zeta potential is observed in the presence of CTAB and the mixture of CTAB/TX-100. On the other hand, the addition of anionic SDS to

Fig. 9 Zeta potential of the system $\text{MnO}_2/0.01 \text{ M NaCl}$ in the absence and presence of guar gum (1 ppm) and surfactants

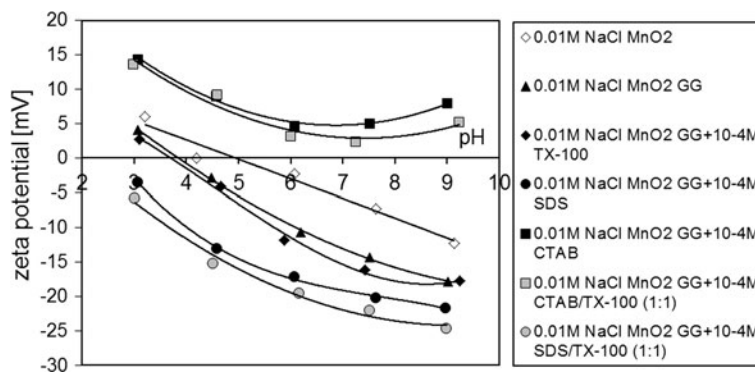
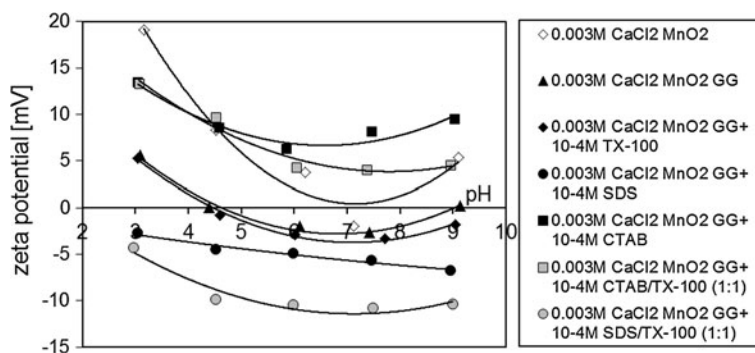


Fig. 10 Zeta potential of the system $\text{MnO}_2/0.003 \text{ M CaCl}_2$ in the absence and presence of guar gum (1 ppm) and surfactants



the adsorption system (with or without nonionic TX-100) results in the decrease of the MnO_2 zeta potential. This decrease is a consequence of two effects. The first one is the presence of the negative charge in the diffused part of the electrical double layer and the second one is the shift of the slipping plane towards the bulk solution, coming from the adsorption of polysaccharide or the polysaccharide/surfactant complex (Chibowski et al. 2000). The above mentioned shift of the slipping plane is larger in the presence of the surfactant mixture than in the presence of the only one surfactant. The adsorption layer created under such conditions (two surfactants exhibit synergetic effect) is more expanded towards the bulk phase and that is why the zeta potential decreases. In the system where only nonionic GG is present or in that with GG and TX-100 the decrease of the zeta potential also results from the shift of the slipping plane caused by the adsorption of polymer or polymer-surfactant-polymer complexes. The comparison between the zeta potential of MnO_2 in the presence of $0.01 \text{ mol dm}^{-3} \text{ NaCl}$ (Fig. 9) and $0.003 \text{ mol dm}^{-3} \text{ CaCl}_2$ (Fig. 10) shows that the values of the zeta potential of MnO_2 obtained in the presence of CaCl_2 are higher than those obtained in the presence of

NaCl , which is typical of these electrolytes but the obtained dependences are very similar.

Conclusions

The obtained results let us draw some conclusions about the influence of the surfactants on the guar gum adsorption on MnO_2 and also on the structure of the formed electrical double layer. Nonionic guar gum interacts with nonionic TX-100 (Triton X-100), anionic SDS and cationic CTAB as well as with the mixtures of SDS/TX-100 and CTAB/TX-100. The latter mixtures are the most effective in increasing the amount of guar gum adsorption on the MnO_2 surface which is a consequence of synergetic effect. Among single surfactant solutions the largest adsorption of guar gum on manganese dioxide was observed when CTAB was added to the adsorption system. This results from strong interaction between the GG macromolecules and CTAB. Guar gum also influences the amount of surfactants adsorption which is the evidence for complex formation.

The formed complexes between at least two macromolecules of guar gum and one (or more) molecules

of surfactants are adsorbed on the surface of MnO_2 in a characteristic way—one macromolecule of guar gum is bonded to the surface and to the surfactant and this surfactant is bonded to another macromolecule of guar gum. Because of such an arrangement surfactants are present in the upper parts of the electrical double layer.

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