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ADSORPTION OF POLY(ACRYLIC ACID) ON THE SURFACE OF TiO_2 IN THE PRESENCE OF DIFFERENT SURFACTANTS

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Abstract. Results presented in this paper consider research on the influence of the presence of surfactants (cationic CTAB, anionic SDS) on adsorption of poly(acrylic acid) (PAA) at the titanium dioxide/solution interface. Research was carried out as a function of concentration of surfactants and the way of introduction of reagents to measured mixtures (PAA-CTAB-TiO_2-NaCl and PAA-SDS-TiO_2-NaCl). In order to compare obtained results of adsorption amount of PAA in mixed systems, measurements of adsorption amount of PAA on titanium dioxide without surfactant addition were also conducted. Observed changes in adsorption amount in the presence of surfactant are a result of an emerging complex polymer-surfactant and competitive adsorption of the two components on the TiO_2 surface.

keywords: adsorption, surfactant, polymer, titanium dioxide, polyacrylic acid

1. Introduction

Adsorptive behaviour of polymer/surfactant mixtures on the interface solid/solution is important not only for industrial but also in household applications. Wide possibilities of application of polymers and surfactants encourage scientists to make research on mentioned high-molecular weight substances. A mechanism of creation of complexes of polymer and surfactants in water solutions is well known. There is much less literature data on such interactions at the interface solid-solution. The problem considers not only competitive adsorption of polymer and surfactant but also adsorptive possibilities of creating complexes polymer-surfactant (Goddard, 1986, Goddard and Ananthapadmanabhan, 1998).

Composition and structure of co-adsorbing layers are dependent on the order in which components of the solution (polymer and surfactant) are added or if the adsorption process is conducted directly from mixtures. Research shows that when sequential adsorption is running, obtained structures that are a result of it are impossible to obtain via normal adsorption (with only one component). Emerging structures of adsorbed by-surface layers significantly influence stability of dispersed systems. This stability is very important not only in paint industry, cosmetics, pharmaceuticals but also in mineral processing. Adsorption of polymers, surfactants or polymer-surfactant complexes can greatly influence surface properties of various minerals. Thus, the process of their separation and enrichment can be conducted with much greater efficiency (Somasundaran et al., 1998; Besra et al., 2002). That is why the aim of present research was to estimate the influence of cationic and anionic surfactant and the order of introduction of separate components (polymer, surfactant) into mixed systems (PAA-CTAB-TiO_2-NaCl and PAA-SDS-TiO_2-NaCl) on the mechanism of adsorption of polymer at the TiO_2/solution interface.

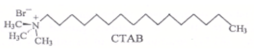
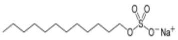
2. Materials and methods

Titanium dioxide P-25 by Evonic was used as adsorbent. TiO_2 P-25 is a mixture of 80% of anatase and 20% rutile. Specific surface of the mentioned oxide measured with the BET method was equal to 64.15 m^2g^{-1}. Poly(acrylic acid) (PAA) by Aldrich, molecular weight (M_w) 60 000 was used as a polymer. Poly(acrylic acid) is a compound which belongs to a group of ionic polymers. It has only one type of functional groups, carboxylic groups, which makes it an anionic polymer.

A solution of poly(acrylic acid) (PAA) was processed by filtration on cellulose membrane produced by Millipore, type YM30 (NMWL: 30 000). Filtration was carried out in order to remove inorganic impurities and eliminate a low molecular weight polymer fraction.

Surface active agents used in the presented research were two surfactants, which characteristics are presented in Table 1. NaCl was used as a background electrolyte.

Table 1. Characteristics of surfactant used (Besra et al., 2002)

Surfactant	Molecular formula	Molecular weight, [g/mol]	Ionic type	Chemicals Structures	Critical micelle concentration (cmc), [mM]
Cetyl Trimethyl Ammonium Bromide (CTAB)	$C_{16}H_{33}N(CH_3)_3^+Br^-$	364.4	Cationic		0.9
Sodium DodecylSulphate (SDS)	n-$C_{12}H_{25}SO_4Na$	288.3	Anionic		8.2

2.1. Adsorption measurements

2.1.1. Calibration curve for PAA/NaCl

In order to obtain adsorption amount of poly(acrylic acid), the method proposed by Crummett and Hummel (1963) was used. Five solutions of electrolyte of $1 \cdot 10^{-3}$ M NaCl and PAA of concentrations from 1 ppm to 200 ppm were prepared. Next, 5 cm^3 of each of the solutions were introduced into volumetric flasks where 1 cm^3 of 20%

NaOH was added and, using various concentrations of HCl, pH was set to a value of 10. One cm^3 of 1% hyamine 1622 solution was then added to such prepared solutions and filled with water up to 25 cm^3. Resulting turbidity was measured after 15 minutes since addition of hyamine, at the wavelength of λ=500 nm.

2.1.2. Adsorption in the PAA/NaCl/TiO_2 system

Ten cm^3 of polymer solution of final concentration equal to 10 ppm, 50 ppm, 70 ppm, 100 ppm, and 150 ppm as well as 10^{-3} M NaCl were introduced to 25cm^3 Erlenmayer flasks. Next 0.04g of titanium dioxide was added. The Erlenmayer flasks were shaken for 24 hours at 25°C. After this time, suspensions were centrifuged, 5cm^3 of the clear solution was taken and concentration of the polymer measured according to the above procedure. The difference between absorbance for pure PAA (calibration curve) and absorbance after the adsorption process of PAA onto TiO_2 was calculated and adsorption amount was the result of those calculations.

2.1.3. Adsorption in mixed polymer-surfactant systems

The measurement of adsorption of PAA and surfactant onto the surface of TiO_2 was conducted in the same way as described above. The only difference was the addition of either cationic (CTAB) or anionic (SDS) in such an amount that a final concentration of the surfactant was $1\cdot10^{-5}$ mol/dm^3 and $1\cdot10^{-4}$ mol/dm^3.

3. Results and discussion

3.1. Adsorption measurements in the PAA-TiO_2-NaCl system

An analysis of adsorption isotherms of poly(acrylic acid) onto titanium dioxide (Fig. 3) showed that mentioned PAA has a significant polydispersity degree. The measure of polydispersity of a sample of polymer is called the polydispersity index (PI), which is defined as a ratio between the average molecular mass (Mw) and average number molecular mass (Mn). For monodisperse polymers (PI equal to 1) the adsorption isotherm is ideally sharp. It is characterized by a sudden increase of adsorption at very low polymer concentration and shows a distinctive plateau in a broad range of concentrations (Santhiya et al., 1999).

The shape of the adsorption isotherm (Fig. 1, rounded shape, no plateau) provides information that in the analysed systems the PI index was much greater than 1.

In research concerning adsorption process of polymers it is essential to take into account pH. Previous research (Somasundaran et al., 1991) showed, that amount of adsorbed polymer is dependent on the change of pH, the change of surface groups of the adsorbent, degree of dissociation of functional groups present of macromolecules as well as conformation changes in polymer chains.

Figure 2 presents an influence of pH on adsorption amount of poly(acrylic acid) onto titanium dioxide.

An analysis of the data presented in Figure 2 shows a significant decrease of PAA adsorption with increasing pH of the solution. Observed decrease of adsorbed amount of poly(acrylic acid) with increasing pH of the solution is a result of the increase of degree of ionization of carboxylic groups in the PAA chain. Macromolecules of PAA ($pK_a = 4.5$) (Gebhard and Fuerstenau, 1983) in acidic environment, up to pH=4.5 have mostly undissociated –COOH groups. With increasing pH, the amount of dissociated –COO- groups in the polymer chain increases, which makes interaction between polymer and more negatively charged titanium dioxide surface even harder. As a consequence of this fact, a decrease of adsorption of PAA is observed.

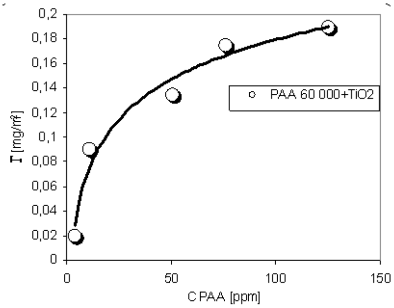


Fig.1. Adsorption isotherm of poly(acrylic acid) (PAA) onto titanium dioxide (natural pH, 10^{-3} M NaCl)

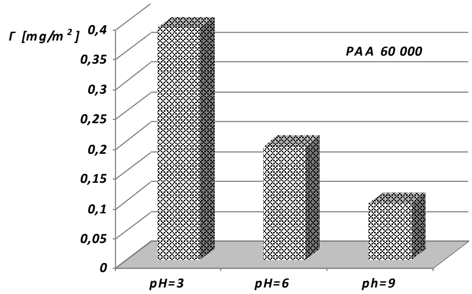


Fig. 2. Adsorption amount of PAA onto TiO_2 as a function of pH in solution of NaCl ($C_{NaCl}=10^{-3}$M, C_{PAA}=100ppm)

An existence of adsorption of PAA at pH higher than pH_{pzc} (pH_{pzc} for TiO_2=6.3) indicates that in this pH range adsorption of a polymer is caused mostly by specific interactions. At pH lower than pH_{pzc}, besides interaction of hydrogen bonding type, a significant role is played by electrostatic interaction between $-TiOH_2^+$ groups and still ionized $–COO^-$ groups, which are still present although not in great amount, in a chain of PAA. As a consequence, the highest adsorption of PAA is observed at pH lower than pH_{pzc}.

Table 2. Dissociation of PAA and the concentration of surface groups of TiO_2

pH	$[COOH]/[COO^-]^a$	Concentration of surface groups^b		
		$- TiOH_2^+$	$- TiO^-$	- TiOH
3	31	32	0.002	179
4.5	1	16	0.003	162
6	0.031	4.4	0.01	156
9	0.000031	1.3	0.11	133

[a] Values of log(α/(1-α) calculated from classical dependency pH – pK_a (Pettersson et al., 2000)

[b] Data calculated from numerical optimization of electrical double layer model (Davis and James, 1978).

Table 2 presents dissociation degree of PAA with increase of pH of solution, as well as calculated values of concentration of surface groups of titanium dioxide expressed in [μC·cm^{-2}], (C_{NaCl} 1·10^{-3} mol·dm^{-3}) versus the pH of a solution (C_{NaCl} =1·10^{-3}mol·dm^{-3}).

Because of high concentration of surface groups -TiOH (Table 2) no matter what pH is used, one might say that those groups are very important in adsorption of poly(acrylic acid) onto TiO_2. In reality, PAA macromolecules adsorb on the surface of titanium dioxide interacting with –TiOH surface groups via hydrogen bonding (Xu and Vasudevan, 1991).

3.2.Adsorption measurements in mixed systems: polymer–surfactant onto TiO_2

Literature data bring information that type of interaction in mixed systems polymer-surfactant is dependent only on character of reagents. If both components, i.e. polymer and surfactant are ionic, a process of their interaction might be dependent on electrostatic interactions, repulsing and attracting (Somasundaran and Krishnakumar, 1998). One might say, that these interactions may significantly influence the process of polymer or surfactant adsorption when this process is conducted from mixed solutions. Adsorption measurements conducted in such systems are performed to get answer to the question whether and how the order of addition of components to the mixture and type of used surfactant influence the amount of adsorption of poly(acrylic acid) at the titanium dioxide-aqueous solution interface. The obtained results were place in Figs. from 3 to 6. They presented adsorption data for mixed systems (PAA/CTAB/TiO_2/NaCl and PAA/SDS/TiO_2/NaCl). Adsorption of poly(acrylic acid) (PAA/TiO_2/NaCl) is also presented.

3.3. Simultaneous addition of reagents to investigated PAA-CTAB -TiO_2 and PAA-SDS-TiO_2 systems

Figures 5 and 6 present the influence of concentration of measured surfactants (CTAB and SDS) on adsorption amount of poly(acrylic acid) on titanium dioxide, when the polymer and surfactant were introduced to a system simultaneously. Measurements were done at pH = 6. When reagents were introduced simultaneously to the mixed systems (PAA-CTAB-TiO_2 and PAA-SDS-TiO_2) at a constant (100 ppm) polymer concentration and changing concentrations of surfactants, adsorption amount of PAA on titanium dioxide compared to the adsorption amount of PAA on titanium dioxide without surfactants was lower for both used surfactants. A decrease of PAA adsorption on TiO_2 of approximately 35% was recorded in presence of CTAB and SDS with their concentration equal to 1·10^{-5}M and approximately from 15 to 20% decrease of adsorption of PAA for higher concentration of surfactants (1·10^{-4}M).

The observed decrease of adsorption of PAA on TiO_2 (Figs. 3 and 4) in presence of analysed surfactants (cationic CTAB and anionic SDS), while both polymer and surfactant were introduced to the system simultaneously is a result of a competitive adsorption of created complexes between polymer and analysed surfactants and free, non-bonded, molecules of CTAB or SDS.

Competitive adsorption results in a blockade of the active sites on the surface of titanium dioxide, which results in lower adsorption of PAA in the presence of analysed surfactants. The conducted measurements show that creation of PAA-CTAB complex and PAA-SDS complex begins with concentrations of surfactants equal to approximately $5\cdot10^{-5}$ M and $1\cdot10^{-4}$ M, respectively. Efficiency of creation of complexes increases with the increase of surfactant concentration. The obtained results of adsorption amount of PAA from pure solutions of PAA and mixed solutions may suggest that the non-bonded surfactant has a greater tendency to block active sites on the surface of TiO_2 than the created polymer-surfactant complexes. As a result of that, at lower concentrations of surfactant a greater decrease of adsorption of PAA was observed, because at these concentrations the complexes are practically non-existent. What is more, a creation of the PAA-surfactant complex in the bulk solution and its adsorption on the surface of TiO_2 results in a decrease of the amount of polymer from the solution. That is why at higher ($1\cdot10^{-4}$M) concentrations of surfactant a higher adsorption of PAA was observed compared to concentration of $1\cdot10^{-5}$M.

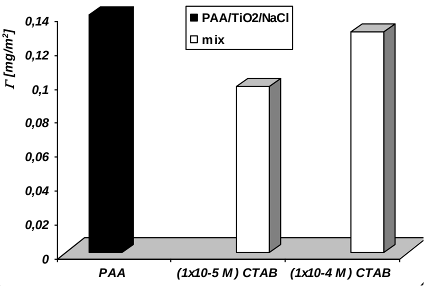


Fig. 3. Adsorption amount of PAA on TiO_2 in presence and absence of CTAB with simultaneous addition of reagents into the system (C_{PAA}=100 ppm). Concentration of NaCl in measured systems was $1\cdot10^{-3}$M

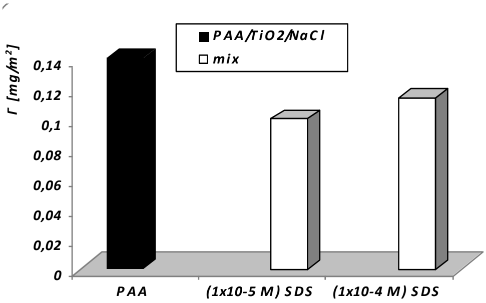


Fig. 4. Adsorption amount of PAA on TiO_2 in presence and absence of SDS, with simultaneous addition of reagents into the system (C_{PAA} = 100ppm). Concentration of NaCl in measured systems was $1\cdot10^{-3}$M

3.4. Influence of the order of addition of adsorbates on adsorption of PAA

A next stage of the research was to analyse the influence of order of addition of adsorbates (polymer, surfactant) into the system and whether this order will have influence on adsorptive behaviour of PAA onto TiO_2. Appropriate data are presented on Figs. 5 and 6.

To understand changes of adsorption of PAA onto TiO_2, Figs. 5 and 6 present data on adsorption amount of PAA onto TiO_2 for both pure PAA/TiO_2 system as well as mixed PAA-SDS, PAA-CTAB systems. An analysis of Figs. 5 and 6 shows that distinct changes of adsorption of PAA onto TiO_2 are a result of both the order of addition of reagents to the system and ionic character of the analysed surfactants.

For a cationic surfactant–anionic polymer system (Fig. 5) there is a significant increase of adsorption of PAA onto the surface of oxide, when surfactant was introduces as first into the system, compared to pure PAA/TiO_2 and when both reagents were introduces simultaneously.

An increase of adsorption of poly(acrylic acid) on titanium dioxide having previously adsorbed cationic surfactant (Fig. 5) is most probably caused by the fact, that in by-surface layer of adsorbed surfactant its concentration is much lower when compared to the bulk solution. As a consequence of that, it leads to more efficient creation of complexes with adsorbed CTAB on the surface of oxide, than it might be observed in the solution. This results in an increased adsorption. The obtained result suggests that previously adsorbed CTAB is a factor that favours adsorption of PAA, and that creation of polymer-surfactant complexes on the surface of solid may take place at much lower concentrations of surfactant when compared to the solution.

Completely opposite results were gained (Fig. 6) for the anionic polymer (PAA) – anionic surfactant (SDS) system. When the first substance added to the system was SDS, and then after reaching equilibrium, a polymer, adsorption of macromolecules of PAA significantly decreased, both compared to adsorption from pure solution of PAA and a mixed PAA-SDS system. In this case the reason for the decreased PAA adsorption on the surface of an oxide with previously adsorbed surfactant is a competitive adsorption of SDS compared to PAA. Previously adsorbed surfactant on the surface of TiO_2 blocks active sites on the surface of the oxide, giving a macromolecule of PAA a more difficult access. Adsorption of PAA by previously adsorbed SDS in not so easy as in the case of cationic surfactant. It is connected with the fact that both SDS and PAA have anionic character, which makes creation of a complex much more difficult. Literature data (Esumi et al., 2000; Fan et al, 1999) prove that anionic polymer-anionic surfactant complexes are created much more difficult than anionic polymer-cationic surfactant. This is proved in analysed systems.

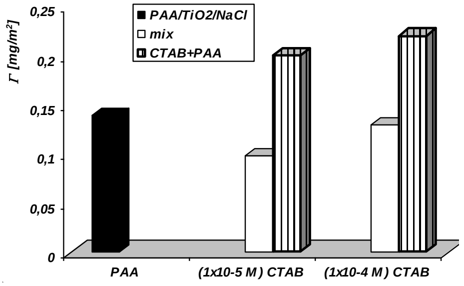


Fig. 5. Adsorption amount of PAA onto TiO_2 as a function of the order of addition of reagents to the system (cationic surfactant – anionic polymer) (C_{PAA}=100 ppm), NaCl 10^{-3}M

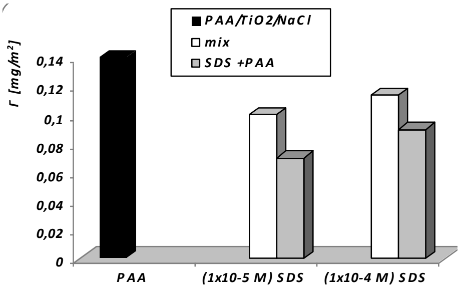


Fig. 6. Adsorption amount of PAA onto TiO_2 as a function of the order of addition of reagents to the system (anionic surfactant – anionic polymer) (C_{PAA}=100 ppm), NaCl 10^{-3}M

4. Conclusions

To sum up, the obtained results on a decrease of adsorption of PAA onto TiO_2 with previously adsorbed SDS follow from a significant blockade of the surface of an oxide by adsorbed molecules of SDS and much less favourable conditions of creation of the PAA-SDS complex.

Generally, one can say, that a presence of an anionic surfactant decreases measured adsorption amounts of anionic polymer on the surface of TiO_2, no matter what was the way of conducting an experiment. A much more beneficial influence on the measured adsorption amount of PAA onto the surface of titanium dioxide was noted for the cationic surfactant – anionic polymer system, but only when a surfactant was added as a first component.

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