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# POLYACRYLIC ACID (PAA) ADSORPTION ON ALUMINA (Al$_2$O$_3$) SURFACE. INFLUENCE OF SODIUM DODECYL SULFIDE (SDS) ON ADSORPTION IN PAA-SDS-Al$_2$O$_3$ SYSTEM

Mutual interactions of ionic polymer with ionic surfactant on alumina surface in system PAA/SDS/Al$_2$O$_3$/NaCl solution system were studied. The research was preceded by studies of the polymer and surfactant in aqueous solution. Obtained data were used for explanation of adsorption equilibrium in the alumina - polymer solution system in SDS presence. Mechanism of polyacrylic acid - surfactant interaction on Al$_2$O$_3$ was explained basing on adsorption and surface tension changes measurements of pure and mixed PAA and SDS solutions in studied system. An influence of the polymer molecular weight and surfactant concentration on adsorption equilibrium at metal oxide-polymer-surfactant interface was considered. An essential role of carboxyl groups of the polymer chain was proved in these systems.

*Key words: adsorption, polyacrylic acid, alumina, SDS*

## INTRODUCTION

Systems containing polymer and surfactant often reveal specific adsorption properties and demand research. Their properties find increasing application in many important industrial processes where stabilization or flocculation of high dispersed system takes place. Precise determination of important parameters for these processes demands many studies of these systems such as adsorption and its influence on electrokinetic properties of solid-solution interface, conformation changes of polymer under surfactant influence and mutual polymer-surfactant interactions.

It is well known from literature that ionic and nonionic surfactants behave differently in solution than in mixture with a polymer (Somasundaran et al. 1985,

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1997; Fleer et al. 1993, 1993A; Sastry et al., 1995). Knowledge of interaction responsible for adsorption mechanism in polymer-surfactant system is important from practical and theoretical point of view and needs intense research. In this paper authors aimed to investigate influence of anionic surfactant sodium dedecylsulphate (SDS) on adsorptive properties of anionic polymer, polyacrylic acid (PAA) on alumina surface.

## MATERIALS AND METODS

### MATERIALS AND REAGENTS

As a surface-active compound, the sodium dodecyl sulphate $C_{12}H_{25}SO_4Na$ (SDS) was used and polyacrylic acid (PAA) (molecular weights: 2000 and 240,000) produced by Aldrich was used as a polyelectrolyte. NaCl was used as a background electrolyte.

Alumina, $Al_2O_3$, produced by Merck was applied as an adsorbate. The specific surface area of aluminium oxide, calculated according to the Brunauer–Emmett–Teller method was $161 \, m^2 \, g^{-1}$. Before measurements, $Al_2O_3$ was washed with double distilled water until the conductivity of the supernatant was smaller than $2 \, \mu S \, cm^{-1}$. The average diameter of the $Al_2O_3$ particles, estimated by scanning electron microscopy was 450 nm. All particles were spherical.

### ADSORPTION STUDY

Adsorption of PAA on $Al_2O_3$ surface performed from the pure solutions of the polymers and mixed PAA-SDS solutions on the $Al_2O_3$ surface was carried out using the static method (Cibowski and Krupa, 1999, 2000) as follows. $Al_2O_3$ was added into the Erlenmeyer flask, which contained $10 \, cm^3$ of the analyzed solution (specified pH, concentration of the polymer and electrolyte). The obtained suspensions were shaken for 24 h. Then alumina was centrifuged and $5 \, cm^3$ of the supernatant were taken for the further analysis. The adsorption was calculated from the difference between the PAA concentration before and after the adsorption ($c_{eq}$, wt. ppm), using the reaction between polyacrylic acid and hyamine proposed by Crummett and Hummel (Crummett, Hummel 1963). The opacity which increases after hyamine addition to the solution was measured colorimetrically using a spectrophotometer (Specord M42, Carl Zeiss) with a special computer program M500. The used wavelength was 500 nm.

### VISCOSITY MEASUREMENTS

The thickness of PAA adsorption layer ($\delta$) was also measured by the viscosity method (Pandou and Siffert, 1987; Wang and Audebert, 1988), using a rotation rheometer. For this purpose, the $Al_2O_3$ suspensions of various volumetric fractions ($\Phi_0$) were prepared. The volumetric fraction of the solid was determined from the formula:

$$\phi_0 = \frac{m}{dv}$$

where $m$ is the solid mass, $d$ the solid specific gravity and $v$ is the reference solution volume.

Next, the suspensions were shaken for 24 h and their viscosity ($\eta$), as well as that of the reference solutions ($\eta_0$) were measured using a rotation rheometer. In this way, the dependence of $\eta/\eta_0$ on $\Phi_0$ (volume fraction in the absence of the polymer) was plotted (calibration curve). In the same way, the viscosity of the suspensions with the adsorbed polymer ($\eta_p$) as well as that of the polymer solution ($\eta_{p0}$) was measured and the ratio $\eta_p/\eta_{p0}$ was determined. Next, the volumetric fraction of the solid in the presence of the polymer ($\Phi_p$) was estimated from the calibration curve. When the radius of the Al₂O₃ particles is known, the thickness of the adsorption layer can be calculated from the following formula:

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

where $r$ is the radius of a metal oxide particle.

The measurements of the thickness of the polymer adsorption layer were performed at volume fraction Al₂O₃ ($\phi_0$) equal 0.0126.

## SURFACE TENSION MEASURED

Mutual polymer-surfactant interaction was determined from measurements of the of the surface tension changes of water solutions containing constant concentration of the polymer ($1\times10^{-3}$ g/ml) and various concentrations of the surfactant. The surface tension of PAA-SDS system was measured with thermostated stalagmometer applied "free downfall of a drop" method [Lando Oakley 1967, Pierson Witaker 1976]. All these measurements were taken at 25°C.

## RESULTS AND DISCUSSION

Due to mutual interaction of polymer and surfactant a complex is formed often of much different properties than those of pure substrates. Their interactions may be examined by measurements of surface tension, viscosity, adsorption and electrokinetic changes of solid-solution interface (Somasundaran et al. 1985, 1991, 1997).

ADSORPTION STUDIES OF PAA/Al$_2$O$_3$/NaCl SYSTEM

To explain an influence of SDS on sorptive properties of PAA on surface of Al$_2$O$_3$ one should examine adsorption equilibrium for PAA in the system. Adsorption of such compounds is measured from drop of their concentration from the solution contacted with a solid. Linear, elastic polymer macromolecules may attain various conformations at solid liquid interface therefore there may be various number of segments bound to the surface (Somasundaran et al., 1997).

Usually macromolecules tend to adopt conformation that enables maximal contact of polymer chain with the solid surface. For this reason bonding of the one segment increases probability of the other ones adsorption that results in multi bond formation. Fig. 1. presents adsorption isotherms of polyacrylic acid on alumina for two molecular weights of PAA.
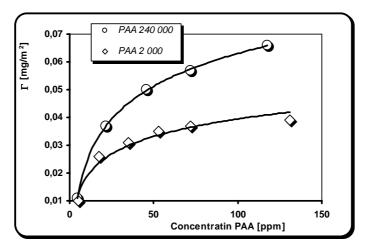


Fig. 1: Isotherms of PAA 2000 and PAA 240 000 adsorption onto Al$_2$O$_3$ at pH 6

One may notice marked influence of the polymer molecular weight on the size of its adsorption. The amount of adsorbed polymer is higher for its higher molecular weight. As mentioned previously polymer macromolecule is bond to the surface of the solid through some number of segments. This number may be the same for various molecular weights of the polymer but total amount of adsorbed polymer is higher for the one of bigger molecule. It may be explained by more loops and tails in interface conformation of the PAA of higher molecular weight. The amount of adsorbed polymer also increases with its concentration. Both effects lead to more compact layer of the polymer with many loops and tails structures of the polymer at the surface and thicker polymer layer.

Obtained adsorption data agree with calculated thickness of the adsorption layer ($\delta$) formed on the surface of the oxide (Tab. 1.).

Table 1. Thickness of the adsorption layer of the polyacrylic acid on the surface of $Al_2O_3$
from the pure polymer and mixed PAA-SDS solutions

| $M_W$ PAA | PAA $C_{PAA}$ [ppm] | PAA $\delta$ [nm] | PAA $\Gamma$ [mg/m²] | PAA-SDS $\delta$ [nm] | PAA-SDS $\Gamma$ [mg/m²] |
|---|---|---|---|---|---|
| 2000 | 50 | 2.34 | 0.032 | 1.98 | 0.025 |
| | 100 | 2.62 | 0.04 | 2.14 | 0.028 |
| 240 000 | 50 | 8.71 | 0.05 | 2.01 | 0.026 |
| | 100 | 9.47 | 0.062 | 2.44 | 0.035 |

The extent of PAA adsorption on metal oxides depends distinctly on pH of the solution. This dependence is well illustrated by Fig.2.
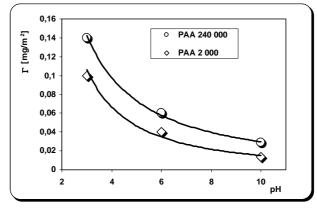


Fig. 2. Adsorption of PAA of various molecular weights as a function of pH of their solution

Generally, amount of adsorbed polymer as a function of pH of the solution depends on both: type of surface group of adsorbent and dissociation degree of carboxyl group of the PAA macromolecule. Total surface charge of the oxide depends on the number of surface forms i.e. - $MOH_2^+$; - MOH and - MO⁻. Along with pH change the dissociation degree of carboxyl groups is changing so is number and type of $Al_2O_3$ surface groups. In Table 2, the dissociation degree of PAA and calculated concentrations of various surface groups of alumina are listed for various pH of the system. Observed decrease of the amount of adsorbed polyacrylic acid produced by increase of pH of the solution is due to increase of the ionization degree of carboxylic groups in PAA chain.

PAA macromolecules, with $pK_a = 4.5$ (Gebhardt and Furstenau 1983), in acidic environment up to pH=4.5 have dominating, non-dissociated –*COOH* groups. When pH increases these groups dissociate to – $COO^-$ ones that increases repulsion with also increasing negative charge on the surface of the solid. As a consequence the adsorption of PAA is decreasing. Noticed adsorption of PAA for pH higher than $pH_{pzc}$, ($pH_{pzc}$ for $Al_2O_3$ =7.9) proves specific interaction between polymer and solid in this

range because due to electrostatic repulsion physical bonding is impossible. This assumption may be supported by analysis of the concentration of various surface groups of alumina listed in table 2.

Table. 2. [COOH] to [COO⁻] group concentration ratio in polyacrylic acid macromolecule and concentration of various surface groups of $Al_2O_3$ in [$\mu C/cm^2$], ($C_{NaCl}=1 \times 10^{-3}$mole$\times$dm$^{-3}$) for various pH of the solution

| pH | [COOH]/[COO⁻][a] | Concentration of groups[b] | | |
|----|------------------|------------|---------|--------|
| | | - $AlOH_2^+$ | - $AlO^-$ | - AlOH |
| 3 | 31 | 0.6 | -1.1 | 105 |
| 4.5 | 1 | 0.4- | -1.9 | 112 |
| 6 | 0.031 | 0.28 | -2.8 | 121.7 |
| 9 | 0.000031 | 0.1 | -7.3 | 120.6 |

[a] Values obtained from the classical relation $pH - pK_a = \log(\alpha/(1-\alpha))$ [Petterson et al. 2000].
[b] The data presented were obtained by numerical optimization of the electrical double layer model (Dawia and James, 1978).

Below $pH_{pzc}$, beside hydrogen bridge type interaction, electrostatic attraction between -*$AlOH_2^+$* and dissociated – *$COO^-$* groups may play important role. As a consequence the increase of PAA adsorption below $pH_{pzc}$ is observed.

Because adsorption of PAA macromolecules takes place at pH range 3-10 and concentration of surface group -*AlOH* is much higher than other ones and pH independent one may assume their dominant role in adsorption process on $Al_2O_3$ surface through hydrogen bridge. Such bonding between hydrolyzed surface of $Al_2O_3$ and polyacrylic acid macromolecule may exist because carboxyl group of the polymer may act as donors or acceptors of protons. A diagram below presents reaction between surface groups of alumina and non dissociated and dissociated carboxyl group of PAA macromolecule.
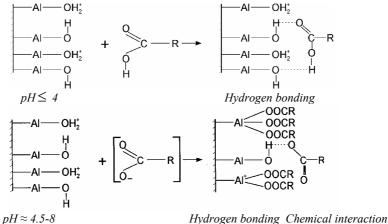


Fig. 3. PAA macromolecule - $Al_2O_3$ surface interaction (Santhiya et al., 19990

Basing on literature (Somasundaran et al., 1985, 1997 1991, 1997A, Santhiya et al., 1999) and own studies concerning PAA adsorption on metal oxide surface we may propose following mechanism of the polymer adsorption on the alumina:

1.  Below pH$_{pzc}$ of Al$_2$O$_3$ (pKa PAA = 4.5) for adsorption process of the polymer with carboxyl groups (*-COOH, -COO$^-$*) of PAA on positively charged alumina surface the hydrogen bonds and electrostatic interactions are responsible;

2.  In pH 4.5 - 8 range (pH$_{pzc}$ Al$_2$O$_3$ = 7.9) beside hydrogen bond a chemical interactions between ionized carboxyl groups and Al ions present on surface of the oxide (Fig. 3). Electrostatic interactions also take place in this pH range.

3.  Above pH$_{pzc}$, for adsorption process of PAA (with almost completely ionized carboxyl groups) on alumina surface (covered predominantly with negatively charged *AlO$^-$* groups) only specific interactions are responsible (hydrogen bridge or chemical reaction between *AlOH* and *–COO$^-$* groups). In this pH range there is no electrostatic interactions and due to there is lowest adsorption of PAA.

### ADSORPTION STUDIES OF PAA/SDS/Al$_2$O$_3$/NaCl SYSTEM

Described above adsorptive behavior of polyacrylic acid on alumina surface is helpful in understanding processes at solid/solution interface in a mixed polymer-surfactant system.

A characteristic feature of surfactants is their ability to decrease surface tension of water. This behavior may be modified by for example polymer addition. Variations of concentration of both polymer and surfactant may vary surface tension of such solution. Final changes depend mainly on mutual polymer-surfactant interactions i.e. type of substances and formation of complexes. Hydrophobic interactions, hydrogen bridge bonds and electrostatic interactions are responsible for behavior of such systems (Somasundaran et al., 1997, 1997; A Santhiya et al., 1999).

In the paper, surface tension measurements of PAA, SDS and their mixtures in aqueous solutions were undertaken to detect polymer-surfactant interaction.
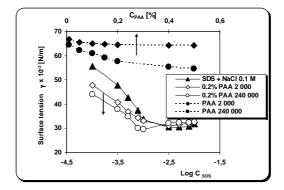


Fig. 4. Surface tension of PAA of various molecular weights versus polymer concentration
[%] (dashed line) and surface tension of mixed PAA-SDS solutions versus SDS concentration
(solid line) in 0.1 M NaCl solution

Figure 4 presents changes of the surface tension of solutions as a function of polymer concentration (dashed lines) and for mixed PAA-SDS solutions as a function of surfactant concentration (permanent line) at constant polymer concentration (0.2%). As may be seen, polymer almost does no not change surface tension of its solutions. In mixed solutions, due to mutual interaction between molecules the polymer-surfactant complexes are formed (solid line in Fig. 4.).

In mixed PAA-SDS system one may notice influence of the polymer molecular weight on lowering of the surface tension. It probably is caused by hydrophobic interactions between PAA and SDS chains, because electrostatic repulsion of negatively charged chains of both molecules makes complex formation impossible (Lang 1971).

Considered above adsorption measurements for mixed PAA/SDS solutions on alumina surface were used to explain described behavior of the system. As can be see in Figs 5 and 6 the presence of anionic surfactant noticeable lowers the amount of adsorbed polymer on $Al_2O_3$ surface.
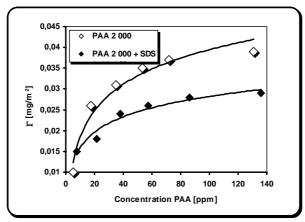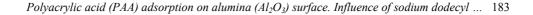


Fig. 5. Adsorption of PAA and PAA-SDS complexes ($M_W$ =2 000) on $Al_2O_3$ surface for PAA/$Al_2O_3$/NaCl and mixed PAA/SDS/$Al_2O_3$/NaCl systems, $C_{NaCl}$=1x10$^{-3}$M; $C_{SDS}$=1x10$^{-4}$M

A dramatic lowering PAA adsorption in the presence of SDS may be attributed to competitive adsorption of PAA-SDS complexes and free SDS that blocks adsorption sites on the alumina surface. Additionally, spacial conformation of PAA-SDS complexes differs much from PAA macromolecules in solution. It results in grater number of interaction points of such complex molecule with functional groups of $Al_2O_3$.

Adsorption of PAA from its solution leads to structure of polymer chain with numerous loops spread to the bulk of solution. Such conclusion may be proved by adsorption layer thicknes measurements on $Al_2O_3$ for pure PAA and mixed PAA-SDS solutions (Tab. 1).
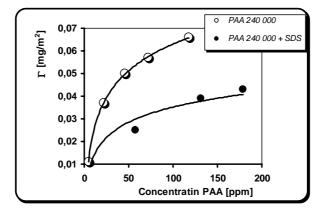
Fig. 6. Adsorption of PAA and PAA-SDS complexes (M$_W$ =240 000) on Al$_2$O$_3$ surface
for PAA/Al$_2$O$_3$/NaCl and mixed PAA/SDS/Al$_2$O$_3$/NaCl systems, $C_{NaCl}$=1x10$^{-3}$M; $C_{SDS}$=1x10$^{-4}$M

As a consequence, flat compact adsorption layer of PAA-SDS complexes decreases adsorption of PAA.

It leads to the mentioned earlier decrease of the adsorption layer thickness. Especially pronounce is this effect for PAA of higher molecular weight.

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**Chibowski S., Pszkiewicz M.,** *Adsorpcja kwasu poliakrylowego na powierzchni tlenku glinu $Al_2O_3$. Wpływ dodecylowego siarczanu sodu (SDS) na adsorpcję w układzie PAA-SDS-$Al_2O_3$,* Physicochemical Problems of Mineral Processing, 40 (2006), 175-184 (w jęz. ang.).

Polimer i surfaktant oddziałując ze sobą tworzą kompleks, którego własności często różnią się znacznie od własności czystych składników. Te wzajemne oddziaływania można badać mierząc takie wielkości jak np.: napięcie powierzchniowe, lepkość, adsorpcję czy też zmiany elektrokinetyczne granicy faz ciało stałe-roztwór**.** W pracy podjęto próbę opisu mechanizmu adsorpcji kwasu poliakrylowego (PAA) na powierzchni tlenek glinu w obecności i pod nieobecność dodecylowego siarczanu sodowego (SDS).Opierając się na badaniach własnych oraz doniesieniach literaturowych dotyczących adsorpcji PAA na powierzchni tlenków metali zaproponowano mechanizm adsorpcji polimeru na powierzchni $Al_2O_3$. Przeprowadzone pomiary adsorpcji w układzie mieszanym PAA-SDS na powierzchni $Al_2O_3$ wykazały, że w obecności anionowego surfaktantu następuje wyraźny spadek ilości zaadsorbowanego polimeru. Powodu wyraźnego obniżenia się adsorpcji PAA w obecności SDS należy szukać zarówno w konkurencyjnej adsorpcji niezwiązanego w formę kompleksów dodecylowego siarczanu sodu jak również utworzonych kompleksów PAA-SDS.