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ORIGINAL CONTRIBUTION

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Adsorption of polyacrylic acid on hydrophobic and hydrophilic surfaces

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Abstract In this paper the adsorption of polyacrylic acid ($MW = 5000$) on the hydrophobic mercury surface and on the hydrophilic γ-Al_2O_3 surface at pH = 3–4 in 0.55 M sodium chloride solution was investigated. Measurements of change of the double layer capacitance by phase selective a.c. voltammetry were used for determination of the adsorption of polyacrylic acid on the mercury electrode. The same method was used for the determination of the polyacrylic acid remaining in the solution after the adsorption on hydrophilic particles (γ-Al_2O_3 particles). The results obtained for adsorption of polyacrylic acid were compared to the results of the adsorption of humic substance of similar molecular weight under similar experimental conditions. The study has shown that polyacrylic acid in acidic solution is strongly adsorbed on the mercury surface, which is comparable to the adsorption of humic substance on the mercury surface. At the same time, the adsorption/deposition of polyacrylic acid on the γ-Al_2O_3 surface is weaker compared to humic acid, indicating at a smaller degree of interaction of polyacrylic acid with aluminium ions and with hydrophilic surface.

Key words Polyacrylic acid – γ-Al_2O_3 – mercury surface – adsorption – voltammetry

Introduction

Poly(acrylic acid)s (PAAs) are well defined polymeric substances with polyelectrolyte properties that can be used as model compounds for the study of natural biogeopolymers such as humic substances [1, 2] which constitute a major part of the organic material present in natural waters. Compared to humic substances, which contain various functional groups, polyacrylic acids are much simpler molecules, containing only carboxylic groups and linear $-CH_2-CH_2-$ chain, which facilitates the distinction between the groups involved in the interaction with hydrophilic or hydrophobic surfaces. In the case of hydrophobic mercury surface, it has already been found that polyacrylic acids are strongly adsorbed at low pH values and not adsorbed at all [3] at high pH values [3]. It was also found that the polyacrylic acid with higher molecular weight is not necessarily more strongly adsorbed when calculated on the monomer unit (acrylic acid), as it is assumed that only segments of polymeric molecule are adsorbed. This is in accordance with the results of Miller and Graham, who in their early paper [4] found that the adsorption energy of a polymeric molecule (polymethacrylic acid) was built up additively from the adsorption of segments of molecule.

The adsorption of various organic molecules on mineral surfaces was investigated as well [5–11]. Some models describing adsorption of solutes to different mineral surfaces are available for carboxylic acids [5, 6], N-heterocyclic aromatic compounds [10], and substituted nitrobenzenes and nitrophenols [11]. The sorption behaviour of dissolved humic substances on mineral surfaces [12, 13] and the sorption of hydrophobic organic compounds on mineral bound humic acid have been investigated [14]. The sorption of organic compounds to humic substances as a substrate was also investigated [15].

Under conditions of high ionic strength and low pH of the solution, the humic acid undergoes coiling due to the neutralization of the charge repulsion between adjacent carboxyl or hydroxyl groups on the humic substance [13]. The sorption of the coiled humic substance might be similar to that of an uncharged polymer which displays loop and tail formation [4, 16, 17] with a few attachment points to the mineral surface.

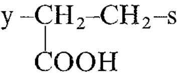
Pefferkorn et al. [7–9] studied different modes of interaction of polymers and polyelectrolytes with partially soluble and nonsoluble colloids, particularly with aluminium oxide (at pH 5 and 4). They found that adsorption or deposition (for fully complexed polyelectrolyte) on soluble oxides was induced by polyion complexation with dissolution species – in their case aluminium ions. They found two different situations regarding the kinetics of adsorption/desorption. For low polymer/aluminium ion ratio, the polymer was rapidly adsorbed while for high polymer/aluminium ion ratio the adsorption was long delayed.

Research of the adsorption of polyelectrolytes and humic substances on mineral surfaces has focused on the effects that pH, ionic strength and presence of cations exert on their configuration, influencing at the same time their adsorption. Foissy et al. [16] found that the forces leading to adsorption of the polymer molecule (polyacrylic acids of $MW = 4000$, 2000 and 700) are not of the same type at the alkaline and at the acidic pH. At intermediate pH, where attractive electrical forces are of major importance, the configuration of the adsorbed molecules depends on the polymer concentration in the solution. In the presence of calcium ions, at alkaline pH, the adsorption is enhanced due to the decrease of electrical repulsions.

In the paper by Burg et al. [18], the authors examined the forces acting between negatively charged muscovite mica surfaces immersed in solution containingNaPAA (sodium salt of PAA). No evidence for PAA adsorption in the absence of calcium ions in the solution was found, however, in the presence of calcium ions the adsorption was significant.

Ochs et al. [12] studied the adsorption of humic acid onto the hydrophobic mercury surface and γ-Al_2O_3 particles. They found that HA is strongly adsorbed over a wide pH-range; hydrophobic interaction prevails at the mercury surface while coordinative adsorption (ligand exchange) is predominant at the oxide surface. However, true adsorption equilibrium was not reached within hours. This slow approach to the equilibrium was ascribed to the polydispersity of HA resulting in fractionation process, where fast-adsorbing low-molecular weight compounds are successively displaced from the surface by slow-adsorbing compounds of higher molecular weight, although the authors could not exclude molecular rearrangements of HA-molecules at the interface either.

In this paper we studied the adsorption of polyacrylic acid (PAA) of molecular weight $MW = 5000$ on the hydrophobic mercury surface and on the hydrophilic γ-Al_2O_3, which we compared to the adsorption behaviour of the humic acid of similar molecular weight [12]. Our measurements were done in the concentration range of PAA similar to the concentration of HA in natural waters. Therefore, PAA concentrations were low, and the factors otherwise very important for adsorption of polymeric material (viscosity and aggregation number [19–21] were not pronounced in our case).

Using polyacrylic acid as simple model substance, due to the presence of only  $-\underset{\mathrm{COOH}}{\underset{|}{\mathrm{C}}}\mathrm{H}_2-\mathrm{CH}_2-$segments we expected to be able to distinguish more easily the key factors governing the adsorption processes of polymeric substances on the hydrophobic and/or hydrophilic surfaces.

Experimental

All measurements have been made by using phase selective a.c. voltammetry (PSACV). In phase selective a.c. voltammetry, a direct voltage is applied across the cell (i.e. between working and reference electrode) with superimposed sine-wave alternating voltage of small amplitude [22, 23]. By using this method, either the capacitive current – i_c (i.e. the current needed to built up a certain potential on the electrode) or the Faradaic current i_f (i.e. the amount of current needed for electron transfer at the interface) can be measured selectively since i_c is always shifted by $\varphi = 90°$ with respect to the applied alternating potential, i.e. current and potential are out of phase while i_f is in phase with respect to the alternating potential: $\varphi = 0°$. The capacitive behaviour of Hg/H_2O interface is mainly governed by the dielectric properties of the molecules in the adsorption layer. Organic molecules which adsorb on the electrode have lower dielectric constant than water molecules, causing changes – decrease of the electric double layer capacitance [24]. Total capacitance (c) of the electrode/solution interface is obtained by using the expression:

$$\Theta = \frac{c_0 - c_\Theta}{c_0 - c_{\mathrm{org}}} \tag{1}$$

where Θ is the surface coverage

$$\Theta = \Gamma / \Gamma_{\mathrm{max}} \tag{2}$$

of the electrode with respect to organic adsorbates, and subscripts "0", "Θ" and "org" refer to the surface with no, partial or complete coverage of the electrode with organic molecules, respectively. Further, i_c is directly proportional to c, which gives a direct relation between the phenomenon of investigation, surface coverage (Θ) and measurable quantity (i_c):

$$\Theta = \frac{i_{c,0} - i_{c,\Theta}}{i_{c,0} - i_{c,org}} \, . \tag{3}$$

The experiments were performed with a stationary hanging mercury drop electrode (HMDE) in a three electrode cell (Metrohm VA 663) connected to a Metrohm E-506 polarograph. The phase selective a.c. voltammetry (frequency 75 Hz, amplitude 10 mV, phase angle 90°) was used for measurements of the amount of adsorbed polyacrylic acid on the mercury drop, as well as for the determination of the amount of polyacrylic acid remained in the solution after the adsorption on γ-Al_2O_3. The mercury drop surface area was 5.4×10^{-3} cm^{-2}. Transport to the electrode surface was achieved either by stirring the solution, or by diffusion. Experiments were performed in 0.55 M sodium chloride solution as electrolyte. Sodium chloride salt was purified from organic contaminants by heating the salt at 723 K. After being prepared as a saturated solution (5.5 M), it was further cleaned with charcoal. The measurements were performed at the electrode potential $E = -0.6$ V vs. Ag/AgCl electrode which is close to the electrocapillary maximum of mercury in 0.55 M NaCl solution and favours the adsorption of neutral molecules.

PAA was from Aldrich, p.a. quality, and arrived as a clear, yellowish and highly viscous liquid, containing 50% of solids in water. The stock solutions were made by weighing and diluting with water a certain amount of chemical (usually 2.9 g/L). Al_2O_3 was Aluminium oxide C, Degussa AG, Germany, which was also used in several adsorption studies carried out earlier [6, 12]. The oxide was characterized as nonporous, with an average particle size of 20 nm and a specific BET surface of 100 ± 15 m^2g^{-1}. The concentrations of γ-Al_2O_3 in the solutions were 1–3 g/L.

Equilibrium adsorption experiments with PAA and γ-Al_2O_3 particles were carried out as batch experiments: electrolyte solution (0.55 M NaCl), varying amounts of γ-Al_2O_3 suspension (to make 1–3 g/l), and aliquots of PAA solution were prepared and equilibrated for 20 h on lab shaker, at room temperature. The suspensions were afterwards filtered on prewashed 0.45 μm membrane filters, Millipore, for the determination of the residual PAA by phase selective a.c. voltammetry. As there is always some degree of uncertainty involved in any filtration of polymeric material, the experimental samples were compared to blanks, which were treated in exactly the same manner, except that no γ-Al_2O_3 was added. Adsorption was calculated by (a) an internal comparison to experimental blanks and (b) by determination of the residual PAA using external calibration curve for the same PAA ($MW = 5000$).

Replicate measurements of the solutions did not show any systematic change of i_c even for the lowest concentration of PAA added, hence, the adsorption on the glass walls was negligible.

Results and discussion

In Fig. 1 the apparent adsorption isotherms for polyacrylic acid ($MW = 5000$) for three different conditions of transport to the electrode surface are presented. Depending on the type of transport, the adsorption plateau is established

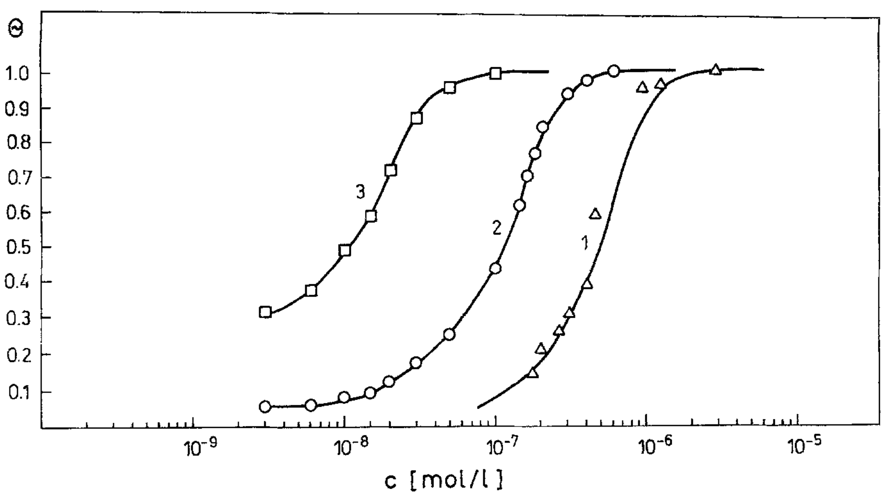


Fig. 1 The apparent adsorption isotherms of polyacrylic acid ($MW = 5000$) in 0.55 M NaCl (pH = 1.8) on Hg-electrode for different accumulation times: (1) 60 s without stirring, (2) 60 s under stirring, and (3) 600 s under stirring, as a function of the bulk concentration. Θ is the degree of surface coverage

at different concentration range of polyacrylic acid. The formation of the adsorbed layer of surface active substances on the electrode surface depends on the kinetics and transport of molecules from the bulk of solution towards the electrode as well as on the kinetics of the adsorption process itself. If the transport of the molecules is a much slower process than the adsorption process, it is the rate determining step. In a quiet solution, the transport of the molecules towards the electrode surface is achieved by molecular diffusion, i.e., it is diffusion controlled. The amount of adsorbed organic substance can be estimated from the results of electrocapillary measurements at a given electrode potential by using thermodynamic method [25]. For this we can use the following equation:

$$\Gamma_i = \frac{-1}{RT}\left(\frac{\partial\sigma}{\partial \ln a_i}\right)_\varphi \tag{4}$$

where σ = interfacial tension, φ = electrode potential, and a_i = activity coefficient of the adsorbing species which varies little with the concentration of the component i. So, the equation becomes:

$$\Gamma_i = \frac{-1}{RT}\left(\frac{\partial\sigma}{\partial \ln c_i}\right)_\varphi \tag{5}$$

where c_i = concentration of the component. The other approach for calculating the amount of adsorbed substance is by electrokinetic measurements [22]. The electrokinetic approach is used very often, especially for substances which are strongly adsorbed at low concentration range. At the electrode there is a decrease in the capacity current, and the coverage of the electrode is not any more the equilibrium one (Θ), becoming Θ_t, depending on time and concentration of the solution. The number of adsorbate molecules (Γ), reaching the interface per unit time and unit area, can be obtained by known relations of the Fick's diffusion laws

$$\frac{d\Gamma}{dt} = D\frac{\partial c}{\partial x} \tag{6}$$

$$\frac{d\Gamma}{dt} = Dc(Dt\Pi)^{-1/2} \tag{7}$$

which, after integration and expressing concentration (c) in mol/l for HMDE gives [22, 26, 27]:

$$\Gamma_t = 11.3 \times 10^{-4}\, D^{1/2}\, c\, t^{1/2}\ (\mathrm{mol/cm^2})\,. \tag{8}$$

The dependence of the adsorbed amount (Γ_t) on the square root of the time of adsorption should be a straight line. The Γ_m value can be determined by introducing the t value obtained at the moment when the saturation value of adsorption ($\Theta = 1$) is attained for the given concentration of the adsorbing substance.

For higher concentrations of polyacrylic acid (greater than 2×10^{-2} g/L) straight lines are obtained for the dependence of Γ_t vs $t^{1/2}$ as shown in Fig. 2 (lines 3, 4 and 5). For the concentration of 5.94 g/L, which corresponds to 1.18×10^{-6} M of polyacrylic acid or 8.25×10^{-4} M monomer units (acrylic acid), the surface concentration (Γ_m) at completely covered electrode was calculated. The diffusion coefficients (D) used for the calculation were taken from the paper of van Leuween et al. [28] as 2×10^{-7} or 5×10^{-7} cm²/s, respectively (there are several diffusion coefficients quoted in that paper, but these two values are mostly cited). Γ_m values calculated with these two different diffusion coefficients are 2.5×10^{-10} mol/cm² and 3.9×10^{-10} mol/cm², respectively which corresponds also to $\Gamma_m = 1.5 \times 10^{14}$ monomer units/cm² or 2.4×10^{14} monomer units/cm², wherefrom we calculated the surface

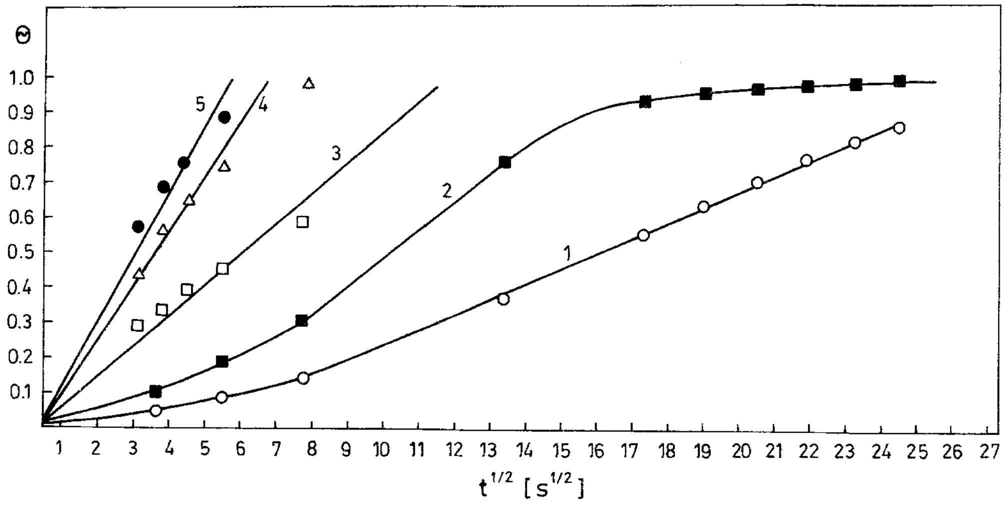


Fig. 2 The degree of polyacrylic acid (MW = 5000) surface coverage (Θ) on Hg-electrode in 0.55 M NaCl solution, pH = 1.8, as a function of square root of accumulation time ($t^{1/2}$) in nonstirred solution. Concentration of polyacrylic acid: (1) 0.75×10^{-3} g/L, (2) 1.5×10^{-3} g/L, (3) 2.2×10^{-3} g/L, (4) 4.3×10^{-3} g/L, and (5) 5.94×10^{-3} g/L

area occupied by one monomer unit (acrylic acid) $A = 1/\Gamma_m$ as 66.6 Å^2 or 41.7 Å^2, respectively.

The surface area of acrylic acid molecule as a whole is 91.8 Å^2 [29], while its hydrophobic part ($-CH_2-CH_2-$) surface area is calculated to be 49 Å^2, which fits in very well with our second calculated value.

As shown in Fig. 2, in solutions with lower concentrations of polyacrylic acid, the dependence of the surface coverage on $t^{1/2}$ is not linear. For the diffusion controlled process, the dependence of $c(\Theta)$ vs $t^{1/2}$ has to be a straight line. If it is not the case, that means that the kinetics of the adsorption process is the rate determining step. When we compared experimentally observed adsorption times for surface coverage $\Theta = 1$ in solutions of lower PAA concentrations to the values calculated on the basis of experiments carried out in higher concentration range, it became obvious that in lower concentration range of polyacrylic acid the total coverage of the electrode surface was achieved in a time shorter than calculated for higher concentration range. For example, the adsorption time for the total surface coverage in the solution of 1.5×10^{-3} g/L, (i.e. 2.08×10^{-5} M monomer units) obtained by using Eq. (8) and the above-mentioned Γ_m (3.9×10^{-10} mol/cm^2) and D (5×10^{-7} cm^2/s) values was calculated as $t = 551$ s. From the Fig. 2 (line 2) it can be clearly seen that for this concentration the total surface coverage is achieved in much shorter time (for line 2 $\Theta = 1$ for $t^{1/2} = 17$, which gives $t = 289$ s instead of the calculated value $t = 551$ s). This may seem strange if we do not take into account the possibility of polymeric molecule to be in a flat position while having enough place on the electrode surface. At higher concentration range, where there is a limited space, the polymeric molecule is in upright position, not having enough space for flat position. These findings fit in well with Hesselink's theory [30] of polyelectrolyte adsorption, where an increase in the dissolved polymer concentration corresponds to the increase in the surface coverage although corresponding to a decrease in the fraction of segments actually adsorbed on it. There are some experimental evidences of such a conformational change along with surface coverage. Norde and Lyklema explain by conformational change the presence of some steps in adsorption isotherms of protein on charged polystyrene [31]. Foissy et al. [16] studied the interaction of PAA with TiO_2 surface, and their experiments also showed that at low surface coverage there is maximum interaction between the polymer functional groups and the surface – a flat configuration. Ochs et al. [12] also observed some steps in the adsorption isotherms of HA on the mercury electrode which can be ascribed to the molecular rearrangement.

Our results could be also interpreted with regard to the theory of Pefferkorn et al., who obtained different adsorption kinetics for the adsorption on aluminium oxide surface depending on the polymer/oxide ratio. They obtained fast adsorption for low ratio and slow adsorption for high ratio which they ascribed to the slow modifications of the electrochemical composition of the suspension. Accordingly, probably also in our case, the adsorption kinetics on the mercury surface could be different regarding different PAA/mercury surface ratios.

From the nonequilibrium adsorption isotherm (Fig. 1, curve 3) we calculated the conditional isotherm parameters. We are aware of the fact that non equilibrium isotherms are nonexistent by definition, but we used the data from nonequilibrium adsorption isotherm (Fig. 1, curve 3, 600 s of adsorption time) according to Frumkin–Fowler–Guggenheim equation (FGG) as we found out that they fitted in very well with the theoretical FGG curve. We have done this just for the purpose to compare approximately our nonequilibrium data with the already existing data for the equilibrium adsorption isotherm of HA [12]. We are also aware that the real comparison would be shown only in the displacement adsorption experiment. So, our comparison is anyhow rather speculative. The adsorption constant for PAA ($MW = 5000$) onto the mercury surface, calculated according to Frumkin–Fowler–Guggenheim equation (FGG) is $\log B = 0.87$:

$$B \cdot c = \frac{\Theta}{1-\Theta} e^{-2a\Theta} . \tag{9}$$

The adsorption constant for HA [12] ($\log B = 2.18$) was calculated for equilibrium conditions which were achieved with long adsorption time ($t = 3600$ s) and with stirring the solution. This could be regarded as an adsorption similar to the adsorption of PAA if we take into account that the results for PAA are nonequilibrium ones for 600 s, and that the result quoted for HA is for equilibrium adsorption obtained for 3600 s. Our data for equilibrium conditions at much longer adsorption time could even more resemble those for HA. At least, our $\log B$ values could not be smaller but only higher – approaching the value for HA. It must be said that for HA a similar adsorption constant is obtained also at higher pH value while, at the same time, polyacrylic acid is not adsorbed in neutral and alkaline solutions. This can be explained by the fact that HA possesses a whole spectrum of different carboxylic, phenolic, sulphur and other groups having different pK values, so that no drastical change in the adsorption of HA by changing the pH value can be expected. In Table 1 we compare the results for the adsorption parameters on mercury according to FGG isotherm. The highest degree of interaction was found for HA.

In Fig. 3 the equilibrium adsorption isotherm for polyacrylic acid on γ-Al_2O_3 is presented. By taking into account the surface area of γ-Al_2O_3 as 100 m^2/g and

Table 1 A comparison of adsorption parameters on the mercury electrode for propionic acid (C_3), PAA (*MW* = 5000) and HA (average molecular weight = 3500) in 0.55 M NaCl solution at pH = 3–4. Adsorption constant (*B*) and the interaction coefficient (*a*) were determined by using FGG equation:

$$B\,c = \frac{\Theta}{1-\Theta}\,e^{-2a\Theta}$$

	log*B* (L mg^{-1})	*a*	Ref.
C_3	– 4.5	0.6	(6)
PAA	0.87	0.82	this work*
HA	2.18	0	(9)

* Apparent adsorption isotherm obtained for adsorption time 600 s.

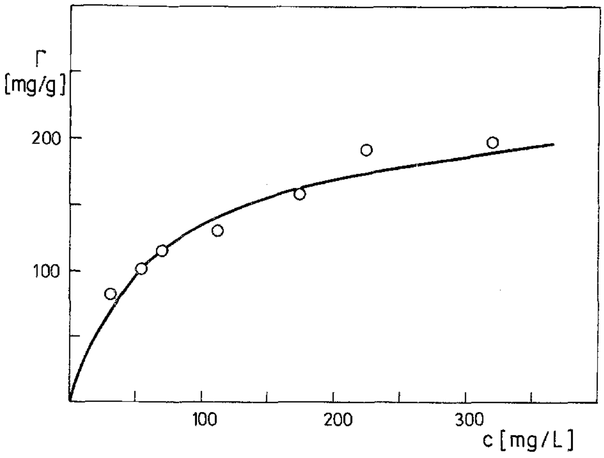


Fig. 3 Adsorption isotherm of polyacrylic acid in 0.55 M NaCl (pH = 4.3) on γ-Al_2O_3 after 24 h of equilibration time. The residual concentrations in solution were determined by a.c. voltammetry. The surface density Γ_{PAA} is plotted vs. the residual concentration of polyacrylic acid. Solid line represents theoretical Langmuir adsorption isotherm and points represent the experimental values

Γ_{max} = 227 mg/g, from the theoretical Langmuirian adsorption isotherm in Fig. 3, we calculated the surface area occupied by one molecule of PAA (*MW* 5000) as 400 $(\text{Å})^2$. We calculated also the surface area occupied by one molecule of HA (from the paper [12]) by taking into account Γ_{max} = 495 mg/g, the average molecular weight of HA as 3500, and the same surface area of γ-Al_2O_3 (100 m^2/g), obtaining the value of 119 $(\text{Å})^2$. At higher pH values (pH = 9.7) Γ_{max} = 200 mg/g, the surface area occupied by one molecule of HA was calculated as 290 $(\text{Å})^2$. Therefrom we can see that the surface area occupied by one molecule of PAA is larger than that occupied by one molecule of HA, which indicates the lower degree of interaction with the mineral surface in the case of PAA. The value for PAA is more similar to the surface area occupied by one molecule of HA at higher pH values. Ochs [12] pointed out as likely that more than two bounds can be formed between an average HA-molecule and the surface. In Table 2, the log*B* values (equilibrium adsorption constants) for HA (from [12]), polyacrylic acid (*MW* = 5000, this paper) and propionic acid (from [6]) are compared.

Table 2 A comparison of adsorption parameters on γ-Al_2O_3 (surface area 100 ± 15 m^2) at pH = 3–4 for propionic acid (C_3), PAA (*MW* = 5000) and HA (average molecular weight = 3500) in 0.55 M NaCl solution

	log*B* (L mg^{-1})	*a*	Ref.
C_3	– 1.869	0	(6)
PAA	– 1.833	0	this work
HA	– 0.869	1.5	(9)

It is obvious that the log *B* values expressed in L/mg for propionic acid and PAA are practically the same, reflecting very similar interaction with the mineral surface regarding propionic acid and monomer unit of PAA. The highest value for log *B* is for HA, which again reflects the possibility of HA to form more coordinative bonds with –OH groups on γ-Al_2O_3 surface, which determines the strength of adsorption on the mineral surface. Our results can also be discussed according to the theory of Pefferkorn et al. regarding the induced adsorption/deposition of polyion complexed with aluminium ions on γ-Al_2O_3. As efficient complexant ions (much more efficient than monovalent or divalent ions), Al^{3+} ions are able to form a complex with propionic acid (C_3), PAA and HA, but again, Al^{3+} ions will have the strongest interaction with the substance possessing the highest amount of complexing sites, which is HA. For PAA and C_3, a similar formation of a complex could be expected regarding the monomer unit of PAA and propionic acid. In our previous paper [3] we also found the strong pH dependence of PAA adsorption on mercury surface. Higher adsorption at low pH values is explained by partial neutralisation of the charges on PAA and can be regarded as complexation with H^+ ions.

Conclusion

Adsorption of polyacrylic acid on the hydrophobic (mercury) surface is the strongest at low pH, which is comparable to the adsorption of humic acid of the similar molecular weight. At the same time, the adsorption on the mineral surface (γ-Al_2O_3), which is governed mainly by the presence of different functional groups capable of forming coordinative bonds or available for complexation with dissolved Al^{3+} ions, is much weaker in the case of polyacrylic acid compared to HA.

The similarities in the course of adsorption of HA and polyacrylic acid onto mercury surface were noticed. For polyacrylic acid, the rearrangements on the mercury surface are indicated by the change in the adsorption process in solutions of different PAA concentrations. It was observed that for higher bulk concentration of PAA there was slow approach to adsorption equilibrium for polymeric substances.

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