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Adsorption of sodium/calcium poly(acrylic acid) salts on anatase: effect of the polyelectrolyte molecular weight and neutralization

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Abstract: Interactions of poly(acrylic acid)s (PAAs) of two different molecular weights (Mw = 9,560 g·mol^{-1} and 4,220 g·mol^{-1}) with surfaces of an untreated anatase TiO_2 were assessed through adsorption isotherm measurements. Those dispersants were tested under different sodium-calcium neutralization states (molar ratio r = Ca^{2+}/CO_2^- varying from 0 to 0.35). Their behavior towards the TiO_2 surfaces can be described by the Langmuir adsorption model. For both polymers, surface coverage (Γ_{max}) evolves linearly with the molar ratio *r*. For a given r value, a lower surface coverage was observed with the polymer having the highest molecular weight. The free energy of adsorption (ΔG_{ads}) of PAAs was estimated from adsorption experiment data. This calculation indicates that sorption occurs spontaneously and is unlikely to be of chemical nature. The absolute values of ΔG_{ads} are higher for the highest molecular weight polymers suggesting that they are more strongly adsorbed to anatase surfaces. The absolute values of ΔG_{ads} per mole of sodium-calcium macromolecules are found to be lower than those calculated for their homologues 100% sodium neutralized suggesting that they are bound with the solid by a fewer number of segments.

Keywords: adsorption, free energy, Langmuir isotherm, sodium-calcium poly(acrylic acid) salts, anatase

1. Introduction

Titanium dioxide (TiO_2) is an important pigment type for paints, varnishes, paper, or plastics and is also needed, for example, in the production of glass, ceramics, and catalysts.

Titanium dioxide is a product of natural origin that forms part of the composition of ilmenite ($FeTiO_3$). In nature it exists in three polymorphic forms: rutile, anatase and brookite.

Only the anatase and rutile crystalline structures are commercially used. Rutile represents the thermodynamically stable polymorph, while anatase, as a metastable phase, spontaneously converts into rutile at temperature above 915°C. The rutile form is a more closely packed structure than that of anatase (Grant et al., 2004).

TiO_2 is obtained from natural raw materials such as ilmenite rocks, ilmenite sands, etc. It is produced in large industrial quantities using two distinct technologies (Braun, 1997):

i. the chloride process (Eqs. (1) and (2)) yields consistently whiter, brighter and purer pigment grades but production of anatase pigment is not possible through this process:

$$TiO_2\ (ore) + 2Cl_2 + C \rightarrow TiCl_4 + CO_2 \tag{1}$$

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2 \tag{2}$$

ii. the sulphate process (Eqs. (3) to (5)) where the production of anatase is possible. This process has more environmental impact due to more waste:

$$FeTiO_3 + 2H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + 2H_2O \tag{3}$$

$$TiOSO_4 + (n+1)\ H_2O \rightarrow TiO_2.nH_2O + H_2SO_4 \tag{4}$$

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$$TiO_2.nH_2O \rightarrow TiO_2 + nH_2O \tag{5}$$

A third-generation process, less expensive and more environment-friendly, was recently developed (Argex, 2015).

Anatase shows less efficient visible light scattering properties. Anatase better supports optical brightening agents (OBAs) as it absorbs less UV light. It is less abrasive than rutile (lower Mohs hardness of 5.5 – 6.0 versus 6.5 – 7.1 for rutile), which is an important property for pigmentation of materials such as fine paper, ceramics and fibres.

The use of predispersed TiO_2 slurry in the paper industry incorporating this pigment either in wet-end or in coatings is preferred as it offers advantages to papermakers as better product uniformity, easy control by flowmeter, etc. Pigment suppliers usually produce high solids content slurries which are compatible with coating make-down (Porter, 1975).

While global consumption of TiO_2 has decreased as alkaline papermaking is growing in volume, the largest industrial application for TiO_2 fillers is in laminate grades for flooring and furniture. In certain white laminates, TiO_2 levels can approach 50 wt.-%.

Proper dispersion of TiO_2 particles in water is a key factor to achieve optimum optical performance (Farrokhpay et al., 2010). Flocculated or agglomerated TiO_2 significantly reduce light scattering performance for delivering opacity (Johnson, 2000). Dispersion properties can be improved by addition of a dispersant. Polymeric dispersants used to disperse titania particles can vary as a function of the considered pigment to disperse (Farrokhpay, 2009). The use of poly(acrylic acid)s (PAAs) to disperse titania pigment is well described (Boisvert et al., 2001). For example, PAAs of low molecular weight are commonly used as dispersants of titanium dioxide (Strauss et al., 1993; Deng et al., 2011; Ran et al., 2007). It is also well known that to produce a concentrated stable anatase suspension, it is necessary to add a polyelectrolyte as a dispersant to make a fluid and pumpable slurry (Heijman et al., 1995; Strauss et al., 1993). The adsorption of PAAs on anatase at neutral to alkaline pHs is endothermic (Lamarche et al., 1982; Foissy et al., 1985) and becomes more endothermic in presence of soluble calcium ions (Böhmer et al., 1994). This endothermic effect implies that the adsorption of PAAs on titania must be accompanied by an entropy gain. The most likely source of entropy gain comes from the release of hydration water of calcium ions specifically adsorbed on the titania surface and/or complexed with polyacrylates (Böhmer et al., 1994). Usually, surfaces of metal oxide in water suspensions are negatively charged at neutral to alkaline pHs and the presence of calcium ions enhances the adsorption of polycarboxylates on aluminium oxide (Vermöhlen et al., 2000) or titanium dioxide (Foissy et al., 1983). It becomes clear that calcium ions play a major role on the polyelectrolyte adsorption process on titania. They lead to the formation of complexes between Ca^{2+} and polyacrylates. On the other hand, they are strongly adsorbed on TiO_2 negative sites. Therefore, the presence of calcium ions at neutral to alkaline pHs has two major effects. They increase the adsorption level of polyacrylates and provide them a higher affinity for the surface of mineral pigments (Foissy et al., 1983; Vedula et al., 1991; El Attar et al., 1985). However, from those previous studies no information about the thermodynamic of the adsorption process was given.

Kostelnik et al. (1995; 1998) found that dispersing agents selected from homopolymers or copolymers of acrylic acid with a molecular weight ranging from 2,000 to 10,000 $g \cdot mol^{-1}$ used in combination with lime allow to produce anatase suspensions having an improved slurry stability and a better tolerance to calcium and magnesium ions. The latter is a key point for paper manufacturers who incorporate titanium dioxide in their coating colour formulations blended with calcium carbonate and used in the paper manufacturing.

Previous works describing the adsorption of PAAs on anatase were conducted using polymers of different molecular weight in a fairly broad range of pHs and the effect of calcium ions was studied after a period of equilibrium and interaction between the surfaces of anatase and PAAs or their sodium salts (Foissy et al., 1983). Commonly, the sodium salts of PAAs in aqueous solution are assumed to have a stretched conformation and are known to have their sodium ions disassociated at a close distance from the negatively charged polymer chains. When divalent cations, as calcium ions, are added in a polyacrylate aqueous solution, these, unlike monovalent cations, are strongly coordinate to the polymer chains. High calcium concentrations in polyacrylate solutions lead to the formation of coils. Therefore, when calcium ions are introduced simultaneously with the polyacrylate molecules (e.g. the addition of a sodium-calcium neutralized PAAs) in an aqueous suspension of anatase, it can be expected that the interactions between the polyelectrolyte and the surface of the mineral are different.

This study aims to have a better knowledge about the interaction between an untreated anatase TiO_2 and two sodium-calcium neutralized PAAs with carboxylic functions neutralized with various amounts of lime. The equilibrium of the adsorption process in a liquid/solid system will be measured according to the Langmuir adsorption model. Data from adsorption experiments will be used to try to provide information on the thermodynamic of the adsorption process (determination of ΔG_{ads}).

2. Materials and methods

2.1. Materials

PAAs were obtained according to a standard polymerisation process. Acrylic acid was polymerized in a 1 L glass reactor using water as a solvent and a red/ox system to initialize the free-radical polymerization of acrylic acid. Water was heated to 97°C. At this temperature, the acrylic acid, the oxidizing and the reducing components were simultaneously added separately into the reactor under agitation. The feed of the components started simultaneously and the feeding time was 2h00. After that time, the injection lines were flushed with water. To complete the free-radical polymerization, temperature in the reactor was kept to 97°C for 30 min. The polymer solutions were then cool down to room temperature before characterization and neutralization.

Their molar masses were measured by Size Exclusion Chromatography (SEC) coupled with a refractometric concentration detector (Waters Corporation, USA).

The liquid elution phase was an aqueous phase (0.05 M of $NaHCO_3$, 0.1 M of $NaNO_3$, 0.02 M of triethanolamine, and 0.03% of NaN_3), which was adjusted to pH 9.0 with 1 N sodium hydroxide solution.

Prior to injection into the SEC column, the polymer solution to be analyzed, was diluted down to a concentration of 0.9 wt.-% in the liquid elution phase, to which 0.04 wt.-% of dimethylformamide was added as a flow marker.

The chromatography device also included an oven. The column was heated to a temperature of 60°C and the refractometer to a temperature of 45°C.

The molar masses and molecular weight distribution of PAAs used in this study are reported in Table 1.

Table 1. Used PAAs of different average molecular masses

polymer sample	*Mw ($g.mol^{-1}$)*	*Mn ($g.mol^{-1}$)*	*Mp ($g.mol^{-1}$)*	*PDI (Mw/Mn)*
PA_{4000}	4,220	1,850	3,380	2.3
PA_{10000}	9,560	3,150	5,980	3.0

Before carrying out any experiment, PAAs were 100% neutralized, i.e. all carboxylic functions borne by the PAA backbones were neutralized either with soda or partially with soda and the rest with lime. Amounts of carboxylic functions (mol.-%) neutralized with lime ranged from 0 to 70 mol.-% as reported in Table 2 which corresponds to a molar ratio $r = Ca^{2+}/CO_2^-$ varying from 0 to 0.35. The aqueous polymer solutions had pHs varying from 8.0 to 8.5 and their concentrations were 35 wt.-%.

As mentioned elsewhere, the precipitation of polyacrylates occurs when *r* reaches 0.37 (Geffroy et al., 2000). The polymer solutions were limpid. They were used without any further purification. Titanium dioxide was a commercial product (TiONA® AT-1) supplied by Cristal. The crystalline form is anatase. According to the supplier, this anatase pigment (TiO_2 content = 98.5%) has no surface treatment. It has a specific surface area (B.E.T., N_2) of 9.9 m^2/g (Gemini VII 2390, Micromeritics), a mean diameter of 385 nm (Zetasizer Nano ZS, Malvern). The pigment isoelectric point (IEP) was found to be at pH = 3.2 (Zetasizer Nano ZS, Malvern using a Laser Doppler Electrophoresis technique coupled with an autotitrator MPT-2 using HCl 0.1N and NaOH 0.1N as titrating solutions – the pH probe was calibra-

Table 2. Characteristics and different neutralization states of the used polyacrylates

polymer sample	*Na neutralization (CO_2H mol.-%)*	*Ca neutralization (CO_2H mol.-%)*	*r = molar ratio Ca^{2+}/CO_2^-*	*specific anionic charge density ($C.g^{-1}$)*
$100PA_{4000}$	100	0	0	1 076
$90PA_{4000}$	90	10	0.05	1 053
$70PA_{4000}$	70	30	0.15	1 044
$50PA_{4000}$	50	50	0.25	898
$30PA_{4000}$	30	70	0.35	816
$100PA_{10000}$	100	0	0	1 310
$90PA_{10000}$	90	10	0.05	1 276
$70PA_{10000}$	70	30	0.15	1 216
$50PA_{10000}$	50	50	0.25	1 095
$30PA_{10000}$	30	70	0.35	1 076

ted with pH 9 & pH 4 buffer solutions before measurements – the ionic strength was fixed to 0.01 mol·L^{-1} with KCl). Although the manufacturer does not claim any surface treatment and the pigment IEP is below pH = 5, it is likely that there is phosphates incorporated in the surface lattice as this is sometimes used to prevent rutile formation.

High purity water was produced by the following sequential treatment: reverse osmosis followed by a two stages of mixed bed ion exchange. Its conductivity was less than 0.1 µS·cm^{-1}.
All other reagents used were analytical grade unless otherwise stated.

2.2. Adsorption isotherms

The adsorption experiments were carried out by mixing anatase in a polymer solution. For the two series, the adsorption isotherm measurements were carried out once. The ionic strength was fixed to 0.01 M using NaCl. The TiO_2 solid concentration was 10 wt.-% (Ø = 0.03). A series of 250 mL solutions were prepared containing various amounts of polymer.

With the help of a mechanical stirrer, the solid was gently dispersed in the polymer solution at 25°C for 24 hours. After that time, pHs of suspensions were controlled. They varied from 7.0 for low polymer concentrations to 7.8 for high polymer concentrations. At those pHs, surfaces of TiO_2 are negatively charged as well as polyelectrolytes which are fully dissociated. The remaining polymer concentration after solid centrifugation was measured in the solution using a carbon analyser (Shimadzu TOC-VCSH). The amount of polymer adsorbed was calculated using the initial and residual polymer concentrations. Calibration curves indicating the evolution of organic carbon levels in water as a function of the polymer concentrations were previously established with known concentrations of different polymers used in this study.

2.3. Anionic charge density of polyelectrolytes

The anionic charge density of polycarboxylate-based superplasticizer is correlated with their adsorption behaviour (Plank et al., 2009). The polyelectrolyte titration is a convenient method that can be applied to measure polymer adsorption isotherms on pigments surfaces (Gaudreault et al., 2009). This method was also used to measure the specific charge density of polycarboxylate ethers using a cationic polyelectrolyte as a titrant reagent. It has been shown that the addition of Ca^{2+} ions causes a decrease of the anionic charge density of polycarboxylates superplasticizers which is the result of strong interactions between Ca^{2+} ions and carboxylate groups through complexation and counter-ion condensation (Plank et al., 2009).

This method is based on the measurement of the streaming current produced by charged macromolecules adsorbed on a moving surface. By adding a polyelectrolyte solution of a known charge density and opposite charge, the neutralization of the polyelectrolyte charge to be determined is obtained by a polyelectrolyte complex formation. This charge neutralization is obtained when the streaming current is equal to zero.

The anionic charge density of the sodium-calcium neutralized polymers was determined using a Mütek particle charge detector PCD 03. The charge detector consists of a PTFE cylinder with an oscillating PTFE piston in the centre. The polyanionic polymer to be analysed adsorbs onto the Teflon surface, while the counter-ions are being separated from the polymer when the piston is moving. This creates a streaming current measured by two platinum electrodes inside the Teflon cylinder. For the polymer titration, a cationic polyelectrolyte (0.001 eq·L^{-1} poly(dimethyl-diallyl ammonium chloride/polyDADMAC) having a molecular weight of about 100 kmol·g^{-1}) was added dropwise into the solution until zero point of charge was reached. For the determination of the polymer anionic charge densities, the ionic strength was fixed to 0.01 M with NaCl, the polymer concentration was 1 g·L^{-1} and pH of the polymer solutions were 8.5 to 9.0 where polyacrylates are fully neutralized.

The experimental specific anionic charge density of the PA_{4000} series and the PA_{10000} series can be calculated according to Equation 6, where *SACD* is the specific anionic charge density (C·g^{-1}), *V* is the consumption of polyDADMAC solution (L), *Cp* is the concentration of polyDADMAC (eq·L^{-1}) and *m* is the weighed mass of the anionic polyelectrolyte to be characterized (g).

$$SACD = \frac{V\,.Cp\,.96{,}485}{m} \tag{6}$$

3. Results and discussion

3.1. Anionic charge density of PAAs

The behaviour of PAAs with respect to mineral surfaces suspended in water depends on different parameters such as the surface charge of the mineral, the ionic strength of the bulk, the presence of multivalent cations, the degree of neutralization of the polyelectrolyte, etc. The latter parameters are known to influence the effective charge of the polyelectrolyte. The values of the anionic charge density of the studied polymers were measured and are reported in Table 2. The neutralisation of the polymers with lime results in a decrease of the specific anionic charge density of the polyelectrolyte which is a function of the ratio $r = Ca^{2+}/CO_2^-$. These results indicate that, for each series, calcium ions interact with both polymers in a similar manner. The fall of the effective anionic charge density with the molar ratio $r = Ca^{2+}/CO_2^-$ is in agreement with the fact that calcium ions induce an entropically driven complexation of carboxylate functional groups and therefore a shielding of the polyelectrolyte negative charges by the closely bound Ca^{2+} ions. This also gives an indication that sodium-calcium neutralized polymers are in all likelihood in a coiled conformation in the bulk solution. PA_{4000} and PA_{10000} were synthetized by means of a free-radical polymerization process in an aqueous medium using chain transfer agents. They are used to reduce the average molecular weight of the final polymer. In the case of PA_{4000}, higher amounts of chain transfer agents are used to lower its average molecular weight. As a result, this lower molecular weight polyelectrolyte comprises a larger proportion of end groups per macromolecules and fewer carboxylic functions borne by the polymer backbone. Therefore, for the same series of neutralization state, specific anionic charge densities of the PA_{4000} series are lower than those of the PA_{10000} series.

From the results of those measurements, it can be expected that the negatively charged TiO_2 surface approach will be favoured as $r = Ca^{2+}/CO_2^-$ increases.

3.2. Adsorption of polymers

Equilibrium adsorption isotherms of polymers PA_{4000} and PA_{10000} on anatase in a 0.01 M NaCl solution are shown in Figures 1 and 2. In all cases, the amount of adsorbed polymer increases with increasing concentration of polymer in the suspension until a plateau is reached.

For both polymers studied, a low adsorption density for sodium polyacrylates at neutral to slightly alkaline pHs is observed. Those results are quite consistent with results reported elsewhere by several authors (Böhmer et al., 1994; Foissy et al., 1983; Chibowski et al., 2002).

Because of the relatively high negative charge number of the titania particles at pHs 7.0 to 7.9, the

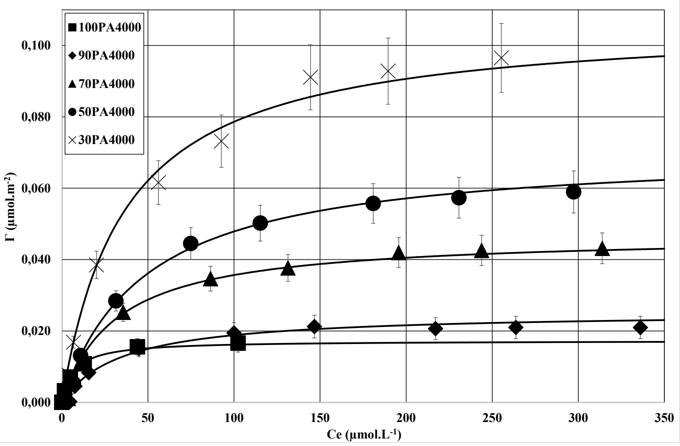

Fig. 1. Adsorption isotherms of polymer PA_{4000} on TiONA® AT with different Na/Ca neutralization, 0.01 M NaCl, pH = 7 to 7.8, T = 298 °K. Lines obtained from the Langmuir equation fit

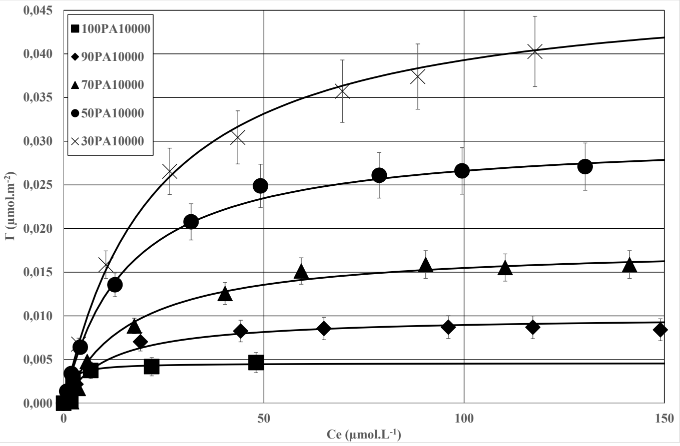

Fig. 2. Adsorption isotherms of polymer PA_{10000} on TiONA® AT-1 with different Na/Ca neutralization, 0.01 M NaCl, pH = 7 to 7.8, T = 298 °K. Lines obtained from the Langmuir equation fit

close encounter near the pigment surface of a negatively charged sodium polyacrylate, bearing negative carboxylate groups, is difficult. The negatively charged polymers 100 mol.-% neutralised with sodium hydroxide ($100PA_{4000}$ & $100PA_{10000}$ in our case) cannot easily approach a globally negative surface close enough to adsorb leading to a low surface coverage density. One might expect long-range electrostatic repulsions between polyacrylate sodium salts and the negatively charged pigment surfaces.

On the other hand we know that multivalent cations like Ca^{2+} ions increase considerably the adsorption of anionic PAAs on metal oxide particles (Grządka et al., 2009) and that Ca^{2+} ions also lead to a strong specific interaction with ionized polymers such as polyacrylates (Pochard et al., 1999; Satoh et al., 1991). The complexation with Ca^{2+} is expected to have a significant influence on the conformation of the polymer as well as on its water solubility (Pochard et al., 2001). Figures 1 and 2 clearly show that the calcium neutralisation of polyelectrolytes enhances the adsorption density of anionic polymers and can be considered as a driving force for the adsorption.

3.3. Langmuir adsorption model

The isotherms can be described by an equation of the Langmuir form (Equation 7) where Ce is the equilibrium polymer concentration, Γ is the loss in polymer concentration due to adsorption, Γ_{max} is the loss in polymer concentration when the surface of titanium dioxide is saturated with a monolayer of adsorbate, and K_L is the Langmuir adsorption constant.

According to Equation 8 deriving from Equation 7, a plot of $1/\Gamma$ as a function of $1/Ce$ will be linear if the adsorption behaviour of polyacrylates is of Langmuir type.

$$\frac{\Gamma}{\Gamma_{max}} = \frac{K_L.C_e}{1+K_L.C_e} \tag{7}$$

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_{max}.K_L.C_e} + \frac{1}{\Gamma_{max}} \tag{8}$$

This calculation shows that the adsorption behaviour of the studied polymers, whatever their sodium-calcium neutralization state, can be described by means of the Langmuir equation (Table 3 with $R^2 > 0.98$).

Values of Γ_{max} (μmol.m^{-2}) were determined from the Equation 8.

Table 3. Maximum adsorption density on titania pigment particles for PA_{4000} & PA_{10000} polyacrylates as a function of their sodium-calcium neutralization state

Polymer sample	Γ_{max} *(μmol.m^{-2})*	$\frac{1}{\Gamma}=\frac{1}{\Gamma_{max}\cdot K_L\cdot C_e}+\frac{1}{\Gamma_{max}}$ R^2	*Polymer sample*	Γ_{max} *(μmol.m^{-2})*	$\frac{1}{\Gamma}=\frac{1}{\Gamma_{max}\cdot K_L\cdot C_e}+\frac{1}{\Gamma_{max}}$ R^2
$100PA_{4000}$	1.73E-02	0.9994	$100PA_{10000}$	4.59E-03	0.9864
$90PA_{4000}$	2.53E-02	0.9960	$90PA_{10000}$	9.94E-03	0.9959
$70PA_{4000}$	4.69E-02	0.9984	$70PA_{10000}$	1.80E-02	0.9960
$50PA_{4000}$	7.09E-02	0.9995	$50PA_{10000}$	3.07E-02	0.9997
$30PA_{4000}$	1.07E-01	0.9990	$30PA_{10000}$	4.82E-02	0.9992

From those results, it is worth underlining that Γ_{max} evolves linearly with the molar ratio r = Ca^{2+}/CO_2^- as reported in Figure 3.

Besides, we can see that Γ_{max} depends on the molecular weight of the polymer which is not in a good agreement with results obtained by Boisvert et al. (2000), who tried to elucidate the adsorption mechanism of sodium polyacrylates on an alumina coated TiO_2 at pH 9. These findings gave results which are similar and of the same order of magnitude than those published by Foissy et al. (1983) who studied the adsorption of PAAs on anatase at pH 9.8. They observed a linear dependence of Γ_{max} as a function of [Ca^{2+}] from 0.025 to 0.125 μmol.m^{-2} with polymers having of average molecular weight of 2,000 and 4,000 g.mol^{-1}. However, this linear dependence was not observed with a PAA of very low molecular weight (Mw = 700 g.mol^{-1}). In addition, we can also notice that results of a study carried out elsewhere and dealing with the adsorption of PAAs onto the surface of titanium dioxide nanoparticles showed that the increase of the polymer molecular masses leads to the increase of the polymer adsorption (Liufu et al., 2005) which is not the case in our study.

Moreover, it is known that the entropy driven formation of a complex between Ca^{2+} ions and CO_2^- leads to chains that are more "hydrophobic" or at least less soluble in water (Lages et al., 2007).

Therefore, in our opinion, driven by an entropy factor, the calcium-polyacrylate complex moves from the bulk phase to titania surfaces. While approaching the pigment surfaces, calcium ions can act as a bridge between the negative sites of the titania surfaces and the negative carboxylate groups of the polyacrylates.

The main reason for that entropy increase is that water molecules from the sphere of hydration of the sodium-calcium neutralized polymer are released during the adsorption process. In addition, it is known that an increase of calcium ions in polyacrylate solutions leads to formation of coils (Schweins et al. 2001; Schweins et al., 2003). This change in conformation from extended (sodium neutralized polymer) to a more coiled conformation (sodium-calcium neutralized polymer) leads to a decrease of the polymer gyration radius.

This conformation change, forming polymers of smaller radius of gyration, is due to a decrease in the repulsion between the carboxylic functions borne by the polymer chains resulting from their charge neutralization (Bulo et al., 2007; Huber, 1993). This calcium-induced shrinking effect can be expected to be stronger when the molar ratio r = Ca^{2+}/CO_2^- increases which contributes to the increase of the polyelectrolyte adsorption density (formation of bidentate complex which might lead to intramolecular bridging which further decreases the coil dimensions).

Because of the fact that, for given experimental conditions, the number of titania surface active sites is constant, an increase of the amount of carboxylic functions neutralized with lime (increase of the molar ratio $r = Ca^{2+}/CO_2^-$) leads to an increase of the possible numbers of specific binding sites of the polymer to titania surfaces and also leads to a specific polymer conformation beneficial to a higher adsorption density of the polyelectrolyte. It results that maximum adsorption evolves linearly with the molar ratio *r*.

Considering that polymers of high molecular weight have higher hydrodynamic radius, the number of adsorbed molecules of the highest molecular weight PA_{10000} polymer is lower which, for a given molar ratio *r*, leads to a lower adsorption density of this polyelectrolyte on titania surfaces.

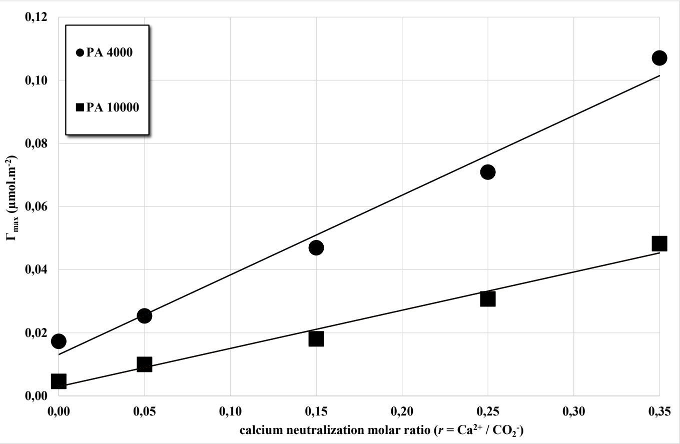

Fig. 3. Evolution of Γ_{max} as a function of the sodium-calcium neutralisation ratio of polymers PA_{4000} or PA_{10000}

3.4 Free energy of adsorption (ΔG_{ads})

Adsorption isotherms describe the phenomenon governing the retention of a substance from the aqueous media to a solid phase. The Langmuir equilibrium constant K_L provides an indication of the affinity of the polymer for the titania surface and can be used to give an estimation of the free energy change of adsorption ΔG_{ads} given in Equation 9 where *R* is the universal gas constant (8.314 J.mol^{-1}.K^{-1}), *T* is the temperature in Kelvin degree and *K* the equilibrium constant.

$$\Delta G_{ads} = - RTlnK \quad (9)$$

As the unit for ΔG_{ads} is J.mol^{-1} and since the unit for *RT* is also J.mol^{-1}, the K value must be dimensionless. If adsorption was investigated from aqueous suspensions and if K_L is given in dm^3.mol^{-1}, Milonjić (2007) suggests calculating the ΔG_{ads} value from Equation 10.

$$\Delta G_{ads} = - RTln(55.5K_L) \quad (10)$$

The free energy of adsorption of polyelectrolytes (ΔG_{ads}) were calculated from adsorption isotherm dataset using Equation 10. Table 4 shows the calculated values of the different adsorption free energies of the polymers studied under the applied experimental conditions.

The adsorption free energy values are in good agreement with results published by Wiśniewska et al. (2009) who studied adsorption and thermodynamic properties of the alumina-poly(acrylic acid) solution systems. The negative sign of the adsorption free energy values indicates that sorption occurs spontaneously and is due to a favourable interaction of polyacrylates with titania surfaces. This adsorption process is unlikely to be of chemical nature as usually the free energy of chemisorption varies from -80 and -400 kJ.mol^{-1} (Anastopoulos et al., 2016).

For a given neutralization state i.e. for a given neutralization molar ratio *r*, we can see an increase in the absolute value of ΔG_{ads} with the molecular weight of the polyelectrolyte giving an indication that the highest molecular weight polymer chains are more strongly adsorbed on the titania surfaces. This is consistent with the fact that macromolecules of PA_{10000} consist of 133 segments in the polymer chain and macromolecules of PA_{4000} consist only of 59 segments. Considering a polyacrylate of a low molecular weight, a smaller number of polymer segments can interact with the TiO_2 surface leading to lower absolute values of ΔG_{ads}.

Results from adsorption experiments taught us that sodium-calcium neutralized polyacrylates are adsorbed in a much larger amounts in all likelihood in a coiled conformation. We can expect that such conformation chains are bonded with the solid by a fewer number of segments and therefore consuming less solid active sites in comparison with the sodium salts of the same macromolecules. Thus, for each series, the adsorption free energy per mole of sodium-calcium neutralized macromolecules are lower than those of sodium neutralized polymers.

Table 4. Parameters characterizing the adsorption process of PA_{4000} & PA_{10000} polyacrylates on titania pigment particles as a function of their sodium-calcium neutralisation state. C_{NaCl} = 0.01 M, pH 7.0 to 7.9, T = 298 °K

Polymer sample	K_L *(dm³.mol⁻¹)*	ΔG_{ads} *(kJ.mol⁻¹)*
$100PA_{4000}$	1.42E+05	-39.37
$90PA_{4000}$	2.90E+04	-35.42
$70PA_{4000}$	3.17E+04	-35.64
$50PA_{4000}$	2.08E+04	-34.60
$30PA_{4000}$	2.76E+04	-35.31
$100PA_{10000}$	6.99E+05	-43.31
$90PA_{10000}$	9.12E+04	-38.27
$70PA_{10000}$	6.06E+04	-37.25
$50PA_{10000}$	6.48E+04	-36.89
$30PA_{10000}$	4.40E+04	-36.46

4. Conclusions

This work was aiming at trying to better understand interactions of sodium-calcium neutralized PAAs of two different molecular weights with untreated anatase TiO_2 surfaces and also to provide information on the thermodynamic of the adsorption process (determination of the free energy of adsorption ΔG_{ads}). Adsorption at neutral to slightly alkaline pH of such polyacrylates with different sodium-calcium neutralization states were studied.

The adsorption behaviour of those polymers fits well with the Langmuir adsorption model. Their adsorption assessed by calculation of Γ_{max} is strongly dependent on the molar neutralization ratio ($r = Ca^{2+}/CO_2^-$) of the polyelectrolyte. For both polymers, it was measured that the amount of polymer to saturate the surface of titanium dioxide (Γ_{max}) evolves linearly with the molar neutralization ratio ($r = Ca^{2+}/CO_2^-$) of the PAAs.

For a given molar neutralization ratio r, the surface coverage Γ_{max} depends on the molecular weight of the polymer. The polymer of the highest molecular weight led to a lower adsorption density on titania surfaces which can be attributed to the fact that polymers of high molecular weight have a higher hydrodynamic radius which prevents the adsorption of large amounts of macromolecules.

Data from adsorption experiments allowed to give an estimation of the free energy of adsorption for each polymer. The negative sign of ΔG_{ads} values indicates a favourable dispersant adsorption on the untreated anatase surfaces. For a given molar neutralization ratio r, absolute values of ΔG_{ads} increase with the PAA molecular weight. This could be explained by the fact that more segments per mole of polymer are bound with the solid active sites when the PAA is of higher molecular weight. Compared with 100% sodium-neutralized polymers, we can also suppose that sodium-calcium neutralized polymers are bound with the solid by a fewer number of segments if they kept their coiled conformation from the bulk solution to the surface. For such sodium-calcium neutralized polymers, absolute values of ΔG_{ads} are lower than their homologue 100% sodium neutralized.

Levels of energy change during the polymer adsorption process are rather small, suggesting that this is more likely a physisorption process involving both electrostatic interactions and hydrogen bonds between adsorbate and adsorbent as described by Farrokhpay (2009).

Although the free energy change is an indication of spontaneity of the adsorption process, more investigations are needed to measure other thermodynamic parameters in order to have a complete understanding of the adsorption process of sodium-calcium neutralized PAAs of different molecular weight on untreated anatase surfaces.

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