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Competitive adsorption of PAM and HPAM on Siliceous Material

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ABSTRACT

The present work aims at studying the outcome and kinetics of competitive adsorption between low and high molar mass chains of neutral polyacrylamide (PAM) or partially hydrolyzed polyacrylamide (HPAM) in aqueous solution at the surface of siliceous material. Monodisperse neutral and charged polymers, PAM and HPAM, were synthesized by RAFT/MADIX polymerization and their adsorption alone or in competitive process was studied. The analysis of adsorption measurements were carried out quantitatively by size exclusion chromatography which allows for distinguishing the relative adsorption of the chains depending on their molar masses. The effect of the average molar mass, dispersity as well as the kinetics of the displacement of pre-adsorbed polymer chains onto the surface by longer chains was investigated. We evidenced that both PAM and HPAM exhibit the same trend. Close to surface saturation, the high molar mass chains desorb polymer chains of lower molar mass. Moreover, by mixing different monodisperse polymer we were able to model the behavior of the polydisperse systems usually encountered in practical applications. By following adsorption over time, our results show that while low molar mass polymers diffuse rapidly and adsorb first, they are displaced by high molar mass ones once they reach the surface. This result remains unchanged even if the low molar mass chains are added several hours before the higher ones showing that there is no kinetic limitation to the displacement of low molar mass PAM and HPAM by higher molar mass ones. The understanding and prediction of this complex competitive adsorption behavior over time is of utter importance for the control of the mechanism of action of these polymers notably in industrial processes.

INTRODUCTION

The competitive adsorption of polymers, i.e. the exchange of macromolecules onto solid surfaces, a phenomenon occurring in numerous application where polymer adsorption is involved, has been widely studied since the 1970s. Understanding and controlling the competitive adsorption between polymer chains of different average molar mass is of great interest in lots of industrial processes.

Indeed, polymers, and in particular neutral (PAM) or partially hydrolyzed (HPAM) polyacrylamides are used in a wide range of industrial applications, such as water treatment by flocculation of particles¹, soil stabilization,^{2, 3} agriculture,⁴ cement flow control,⁵⁻⁷ and last

but not least, in the field of enhancement oil recovery (EOR) where acrylamide based polymers are massively used mainly to increase the viscosity of the injected fluid.⁸ The study of competitive adsorption is of particular interest in this last case where PAM or HPAM of very high average molar mass with broad molar mass distributions are involved. Indeed, during oil recovery, injection of such polymers in the injection well leads to a rapid injectivity loss which negatively impacts the process. Despite its tremendous effect on the ability or not to effectively recover the oil from the field, the origins of this injectivity loss such as hydrodynamic retention, mechanical entrapment or adsorption are still a matter of debate. Recently, Bessaies-Bey et al. showed that polymer adsorption is the leading cause for the loss of injectivity sometimes suffered by the oil industry as it can lead to permeability reductions by orders of magnitudes.⁹ Thus, the characterization of the adsorption of PAM or HPAM onto siliceous materials and particularly the competition between polydisperse species is a key point to reduce those perturbing effects. Although, polymer adsorption in general has been extensively studied in the literature both at the experimental and theoretical level, to the best of our knowledge, the competitive adsorption of PAM or HPAM of different lengths on siliceous materials has been never investigated which is surprising considering their intensive use in various industrial contexts.

Concerning the competitive adsorption of polymers having different average molar masses, three main cases emerge from the literature: uncharged macromolecules¹⁰⁻¹⁵ and polyelectrolytes in high¹⁶ and low^{16, 17} salt content medium. Even if it is globally admitted that in the first two cases longer polymer chains preferentially adsorb to the substrate following entropic considerations¹⁸ while in the third case it is the shorter polymer chains that are preferred because the system is then driven by the electrostatic energy balance, some questions remain:

(i) Firstly, regarding the experimental works cited above, the kinetics of desorption/adsorption depends on several parameters such as the average molar mass and the mass dispersity, the structure of the polymer chain, its chemical nature and the mechanism of adsorption. Reported experiments on the adsorption of polyacrylamide on natural quartz revealed that polymer adsorption is due to the formation of multiple hydrogen bonding between the polymer chains and both silanol and aluminol groups present on the natural quartz surface.^{9, 19} Then the repartition and proportion of anchoring sites at the surface of substrate may play a major role on the competition between species. In this particular case, does the adsorption of larger macromolecules still prevail?

(ii) Moreover in EOR applications, most of the so-called polyacrylamides are in fact partially hydrolyzed and weakly negatively charged. In this intermediate case between the neutral polymer and polyelectrolyte case, what is the impact of the average molar mass of the polymer on adsorption keeping the density of anionic groups constant?

(iii) Most of the experimental studies concerning competitive adsorption cited above have been performed in organic solvent with specific conditions which are far from the industrial reality. For instance, in applications concerning PAM/HPAM adsorption to natural quartz, water is the reference solvent which can complicate the system because it interacts both with the polymer and the oxide.

The present work aims at addressing carefully the issue of PAM/HPAM adsorption on silicates by studying the outcome and kinetics of competitive adsorption between low and high molar mass PAM or HPAM in aqueous solution at the surface of model siliceous material. We first present a method of analysis of adsorption experiments based on Size Exclusion Chromatography (SEC) which allows for a quantitative determination of the relative amount of adsorbed polymer chains of different molar masses. Adsorption experiments were performed using monodisperse PAM and HPAM in a broad range of molar masses from 10 to 1000 kg/mol. These polymers, synthesized by RAFT/MADIX polymerization,²⁰ allowed us not only to investigate the adsorption behavior of the polymer alone in solution but also to model the behavior of industrial polymers (high dispersity) by mixing several monodisperse polymers. Finally, we focused on the kinetics of displacement of polymer chains pre-adsorbed onto the surface as a function of the pre-adsorption time.

MATERIALS AND METHODS

Materials. *Siliceous materials.* Crystallized natural quartz (99.5 % SiO₂, 0.5 % Al₂O₃), named Sikaisol was acquired from Sika (Specific area $S=0.56$ m²/g, determined by BET Nitrogen adsorption; bulk density $\rho=2650$ kg/m³; mean particle diameter $D=50$ μ m),

Polymers. Acrylamide (AM) (40 % aqueous solution) and acrylic acid (AA) (99 %) were purchased from Sigma-Aldrich. Well-defined PAMs and P(AM-*st*-AA)s with different average molar masses and anionicity were synthesized by Reversible Addition Fragmentation chain Transfer / Macromolecular design by interchange of xanthates (RAFT/MADIX) polymerization according to a modified version of the protocol we previously reported.²⁰ Using a low molar mass ($DP_n \sim 7$) polyacrylamide macro-RAFT/MADIX agent, the polymerization of Am or Am/AA mixtures was performed at 25 °C at 20 wt% in water for 2h,

using the ammonium persulfate (APS) / sodium formaldehyde sulfoxylate dihydrate redox initiator. The pH of the reaction mixture was adjusted to 6 prior to polymerization. The resulting polymer was freeze-dried before storage in order to remove water and traces of residual monomer. The characteristics of the polymers such as average molar mass, dispersity and the degree of anionicity are gathered in **Table 1**. The synthesized statistical polymers P(AM-*st*-AA) will be assimilated to hydrolyzed polyacrylamide and noted HPAM-X where X indicates the average molar mass (**Table 1**).

Adsorption experiments. 4 g of quartz particles were first mixed in a bottle with 10 mL of polymer solutions with concentrations ranging from 10 ppm to 200 ppm. Experiments were conducted at the pH of pure water in presence or absence of CaCl₂. Adsorption experiments were conducted at a solid/liquid ratio of 0.4. The bottles were left rolling at constant temperature (23 °C) during 2 hours. The quartz particles were then removed by centrifugation at 6000 g for 15 min to extract the interstitial solution. The supernatant was analyzed with one of the methods described below, namely Total Organic Carbon (TOC) and/or Size Exclusion Chromatography (SEC).

Total Organic Carbon (TOC). Total Organic Carbon experiments were performed on a TOC-VCSH (Shimadzu). The TOC analyzer was first calibrated with reference polymer solutions of known concentrations and by analyzing the liquid phase of the quartz suspension without any polymer. By comparison between this reference value and the measured organic carbon amount in the water extracted from polymer adsorption experiments, the amount of polymer adsorbed on natural quartz was computed. This technique assumes that the difference between polymer concentration before and after contact with quartz particles is only owed to adsorption at the surface of particles.

Size Exclusion Chromatography (SEC) and data treatment. Size exclusion chromatography was performed on a Malvern Viscotek TDA 302 system triple detector equipped with three OH-pak SB-806M HQ columns in series and a guard column. The mobile phase is an aqueous solution at 0.2 M NaNO₃ and the flow-rate is 0.7 mL/min. 100 µL of each sample is passed once in the set of columns before detection. The number- and weight average molar masses (respectively M_n and M_w) and dispersity ($D=M_w/M_n$) were derived from a universal calibration curve based on poly(ethylene oxide) standards from Malvern. Compared to TOC analysis, SEC experiments allows both to distinguish and quantify the polymers depending on their average molar mass.

The chromatograms obtained from the measured refractive index as a function of the retention volume are fitted with log normal distribution in order to extract the area under the chromatograms which was further used to estimate the concentration of a given polymer in a solution containing polyacrylamide with different average molar mass.²¹ As an example, a SEC chromatogram of a polymer solution containing PAM-10K and PAM-1000K is shown in **Figure S1** in Supporting Information. The area under each peak can be correlated to its concentration through pre-determined calibration curves.

Table 1: Main characteristics of PAM and HPAM used in this study

Designation	Anionicity (%)	M_w (kg/mol)	M_n (kg/mol)	\bar{D}
PAM-10K	0	17	16	1.04
PAM-100K	0	167	150	1.11
PAM-1000K	0	1284	1222	1.05
HPAM-10K	10	17	16	1.04
HPAM-100K	10	181	166	1.09
HPAM-1000K	10	817	750	1.09

RESULTS AND DISCUSSION

Adsorption of PAM/HPAM on natural quartz

We first quantified the amount of adsorbed polymer on natural quartz of PAM in pure water and anionic HPAM in CaCl_2 solution with TOC experiments. As shown in **Figure 1**, the amount of adsorbed polymer steeply increased with the polymer concentration with values of the initial slope varying from 40 to 300 ml/m^2 characteristic of a high affinity between the polymer and the particle surface.^{22, 23} This increase was immediately followed by an adsorption plateau at high polymer concentration, which corresponds to full surface coverage. It is now well established that the driving force of the adsorption of acrylamide-based polymers on siliceous materials is the formation of multiple hydrogen bonds between the amide groups of the polymers and hydroxyl groups on the silica surface,²⁴ and this adsorption is exacerbated by the presence of aluminol groups.⁹ The amount of adsorbed polymer can also

be impacted by the physicochemical parameters of the polymer/particle system (pH, temperature, ...) and notably the presence of electrolyte in solution which can decrease the solubility of the polymer chains in solution and consequently increase the adsorbed amount. In our two systems, PAM/H₂O and HPAM/H₂O/CaCl₂, both polymer chains are in good solvent as reported in the literature and in **Figure S2** (Supporting information) respectively. At the pH of the suspensions (pH=6), both the HPAM and the silica surface groups are negatively charged. However, during the adsorption of HPAM on natural quartz, the presence of CaCl₂ screens the electrostatic repulsions between the HPAM and the silica surface. Hence, HPAM in CaCl₂ solution behaved, as expected, similarly to PAM in pure water. We moreover note that the maximum adsorption plateau, Γ_{\max} , increases when the average molar mass of the polymer increases as shown in **Figure 1c**. Indeed, for both PAM/H₂O and HPAM/H₂O/CaCl₂ systems, the maximum adsorption value varies as a function of molar mass following a power law with a power exponent of 0.14. This value is consistent with the reported values for uncharged macromolecules adsorbed on silica.^{14, 22, 25}

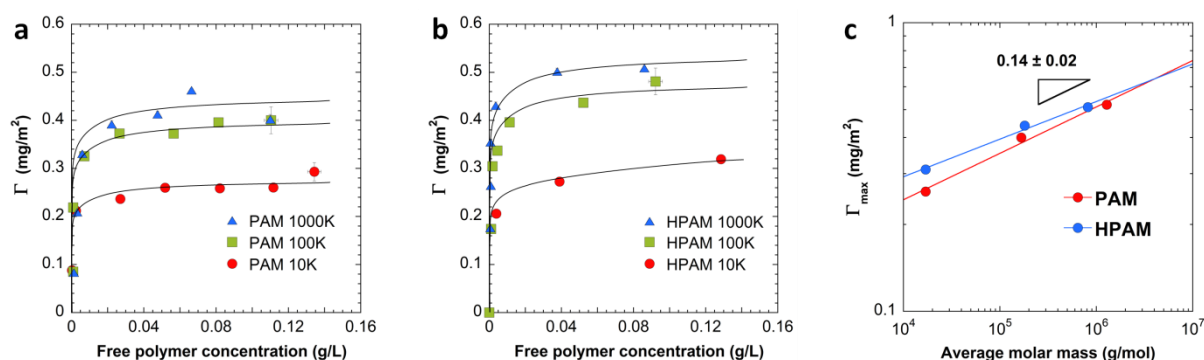


Figure 1: Adsorption isotherms on natural quartz for (a) PAM in pure water and (b) HPAM in CaCl₂ solution ($I=0.035$ M). The lines are guides for the eyes (c) Maximum adsorption amount, Γ_{\max} , as a function of the average molar mass of acrylamide-based polymers.

Mixing monodisperse PAM or HPAM of different average molar masses: Towards a better understanding of competitive adsorption of industrial polymers

This part aims at understanding the effect of the dispersity of industrial PAMs or HPAMs on adsorption by modelling them with a well-controlled distribution of molar masses reconstructed from highly monodisperse batches (see **Table 1**). Experiments were conducted with either a mixture of PAM-10K, PAM-100K and PAM-1000K or HPAM-10K, HPAM-

100K and HPAM-1000K, with the same weight fraction for each component. We chose to study the competitive adsorption of the three polymers by mass and not by number of chains for reasons of SEC sensitivity and viscosity of solution. Indeed conducting the study in terms of number of chains would result in a difference of two orders of magnitude between the mass concentrations between polymers having the lowest and the highest average molar mass. Knowing both M_n and M_w of each polymer, it is possible to compute the dispersity, \mathcal{D} , of the polymer mixtures. Dispersities of 11.4 and 7.9 were targeted, for PAM and HPAM mixture respectively, which is fairly representative of what can be used in industrial applications. The same adsorption protocol as for the individual polymer adsorption experiments was followed. Natural quartz particles are mixed with a solution of polymers mixture of varying concentrations for 24 hours at a solid to liquid ratio of 30 wt%. After centrifugation, the supernatant was then characterized with SEC. **Figure S3** in Supporting information shows the chromatogram of supernatant (i.e. non adsorbed polymer solution) obtained with a refractive index detector for different initial concentrations of PAM-10K, PAM-100K and PAM-1000K mixtures. The fitting of these chromatograms allows to determine the quantities of each mass distribution remaining in solution and consequently the quantities adsorbed onto the surface. Thereby the competitive adsorption of each polymer solutions containing three monodisperse polymers onto natural quartz particles can be plotted. For both polymer mixtures, PAM (**Figure 2a**) and HPAM (**Figure 2b**), the adsorption isotherm could be divided in two parts. First, at low concentrations of polymers, i.e. lower than 0.05 g/L, all species present in solution adsorbed on particles because there is enough space at the particles surface. This interpretation was supported by the chromatograms of the supernatant (**Figure S3** in Supporting information) where no polymers are detected in regards to the detection limits of the SEC technique. As illustrated in **Figure 2a** and **2b**, when increasing the polymer concentration, the adsorbed amount for the two polymers having the lowest average molar masses progressively decreased and tended toward zero while the polymer with the higher molar mass continued to adsorb onto particles until the saturation of the particles surface made it impossible to absorb more polymer chains onto it. In the case of the PAM mixture, we observed that the adsorption of the PAM-1000K reached the same adsorption value, $\Gamma_{\max} \sim 0.5 \text{ mg/m}^2$ as the one obtained by TOC for the polymer alone (**Figure 1a**). However, for the HPAM mixture it is worth noting that the adsorption of HPAM-1000K was significantly lower (0.3 mg/m^2) than the one of the polymer alone, $\Gamma_{\max} \sim 0.5 \text{ mg/m}^2$. A possible explanation would be that the ionic strength was too low to fully screen the particles surface charges as previously reported.⁹ Then, electrostatic repulsion occurred either between the

particle surface groups and the HPAM polymer or between HPAM adsorbed on the particle surface and free HPAM chains thus reducing its adsorption. In any case, the adsorption of polydisperse PAM and partially screened HPAM led to the same behavior, i.e. the adsorption of the polymer chains having the higher molar mass prevailed considerably over the shorter polymer chains present in solution. Nevertheless, as shown the **Figure 2a** and **2b**, for both PAM and HPAM systems some polymer chains with lower molar masses still remained on the surface.

Furthermore, it is also possible to calculate from these data the M_n , M_w and \bar{D} values of the supernatant composition for each concentration of polymer mixtures. To a certain extent, these mixtures model the properties of a polymer with large dispersity during competitive adsorption. The respective evolutions of each parameter are highlighted in **Figure 2c**. At low surface coverage, the supernatant composition was very close from a pure solution of PAM-10K in terms of M_n and M_w , with a dispersity close to 1. Then the dispersity and both the number- and weight-average molar mass of the polymer mixture present in the supernatant increased with concentration meaning that polymer chains having the highest molar mass start to be present in the supernatant. This is due to the fact that the polymer chains with the highest molar mass preferentially impact the weight-average molar mass of the polymer mixture. Finally at higher dosage the macromolecular parameters (M_n , M_w and \bar{D}) tended toward the properties of the initial mixtures (PAM-10K, PAM-100K and PAM-1000K equal in weight proportions) illustrated by dashed lines in **Figure 2c**. This meant that the surface was saturated and the polymer chains with different molar mass were present in the supernatant. These observations were consistent with reported studies showing a modification of the chromatogram of the supernatant after adsorption of polydisperse polymers on silica particles.^{14, 26}

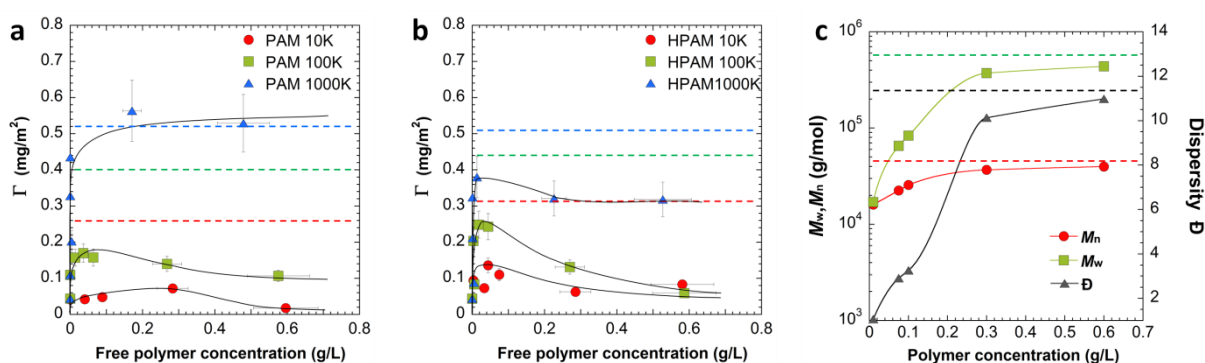


Figure 2: Competitive adsorption on natural quartz of (a) PAM in pure water and (b) HPAM in CaCl₂

solution ($I=0.035$ M) with 24h contact time. The solid lines are guides for the eyes. The dashed lines represent the maximum adsorption value, Γ_{\max} , when the polymer is alone in solution. (c) Evolution of the average molar masses, M_w and M_n , and dispersity \bar{D} of the supernatant during competitive adsorption on natural quartz of a mixture of PAM-10K, PAM-100K and PAM-1000K as a function of the initial concentration of polymers mixture. The solid lines are guides for the eyes. The dashed lines correspond to the M_w , M_n and \bar{D} of the initial polymer mixture.

Adsorption-desorption kinetic aspects

As observed in the previous section, the longer polymer chains, PAM-1000K or HPAM-1000K in electrolyte solution, adsorb preferentially on natural quartz to the detriment of polymer chains of molar masses lower by one or two orders magnitude. However, it should be kept in mind that literature results suggest that regardless of differences in molar masses, kinetics of adsorption/desorption can vary over orders of magnitude depending on the polymer structure, the substrate properties (chemical nature, porosity...) and the resulting adsorption driving force as well as the equilibrium time of the preadsorbed polymer chains. Indeed, Kawaguchi et al. studied by ellipsometry the competitive adsorption onto platinum plate between on the one hand 102 and 775 kg/mol, and on the other hand 422 and 775 kg/mol polystyrene in theta conditions.²⁷ The authors reported that the kinetics of displacement by 775 kg/mol polymer chains of 442 kg/mol polystyrene is slower than for 102 kg/mol. Then, they noted that the displacement of shorter polymer chains is complete after 20h. The same observations have been made by Fu et al. for the competitive adsorption of poly(ethylene oxide) chains having different molar masses on glass.^{12, 28} However, they noticed that short PEO chains become more difficult to displace from the surface when their contact time with the interface or the relative molar mass of the preadsorbed polymer chains is increased.²⁹ Conversely, rapid and total displacement, on the order of several hours, have been also observed in the literature for polystyrene/silica system.^{14, 30} In summary, we can conclude from the literature that the kinetics of displacement of adsorbed polymer chains is highly system dependent.

In this section, we thus report the kinetic aspects of competitive adsorption using SEC experiments either by sequential (i.e. by contacting the surface with the shorter polymer chains during a certain period of time prior to injection of the polymer chains with the higher molar mass) or simultaneous coadsorption of two PAM polymers. By this set of experiments, we tried to answer two questions: How fast does the desorption occurs? And how long does it

take to reach equilibrium? For that purpose, two competitive adsorption experiments were carried out. First, PAM-10K and PAM-1000K were simultaneously put in contact with natural quartz particles at an initial concentration of 0.2 g/L which corresponds to the saturation regime on the particles surface. Then after a time varying from 5 minutes to several hours after addition of both polymers, the samples were centrifugated and the supernatant characterized with SEC. For the second experiment, the short polymer chains, PAM-10K, were first put in contact with natural quartz particles. Thereafter, two different delayed times of addition of the high molar mass polymer PAM-1000K have been investigated to highlight the effect of contact time, i.e. 2 and 24 hours. Afterwards, after 5 minutes to several hours, as in the previous experiment, the samples were centrifugated and the supernatant characterized with SEC. The results are gathered in **Figure 3**.

In the case of coadsorption where both polymers are put simultaneously in contact with natural quartz particles (**Figure 3a**), two regimes were clearly observed. For contact time between the polymers and the natural quartz lower than 30 min, we observed that both polymer chains adsorbed onto the surface. This is due to the fact that shorter polymer chains diffuse much faster than the longer ones and then reach the surface in first.³¹ Then, after around 30 minutes of contact time, the PAM-1000K chains remained adsorbed onto the surface whereas the amount of adsorbed PAM-10K started to decrease. As experimentally reported in the literature by Fu et al. the desorption of short chains from the surface begins only when the mass saturation of the surface reaches the one expected when adsorbing of shorter chains alone, here 0.3 mg/m² for PAM-10K.¹² One hour after the contact time, t_0 , corresponding to the introduction time of PAM-1000K, the maximum adsorbed amount was reached, i.e. 0.5 mg/m². Surprisingly, the desorption of PAM-10K was not complete even after 24 hours. For neutral polymer such as PAM, displacement of short chain polymers was expected since in theory, the free energy of an adsorbed polymer chain is directly proportional to the polymerization degree and consequently to its molar mass.³² For HPAM, electrostatic considerations complicate the matter but, as we have seen above, their behavior in presence of salts is very similar to the one of a neutral polymer due to charge screening. The fact that some short chain polymer remained adsorbed is more puzzling and remains an open question. It could be due to a slow down diffusion of the small polymers in the larger polymer adsorbed layer or to an additional chemical potential term due to polymers concentration near the surface. **Figure 3b** and **3c** show the delayed competitive adsorption between PAM-10K and PAM-1000K, that is when the long polymer chains PAM-1000K were put in contact with a delay time of $t_0=2h$ and $t_0=24h$ after the introduction of the shorter chains. As soon as the

PAM-1000K is added to the sample, PAM-10K started desorbing whereas adsorption of PAM-1000K increased which means that the contact time between PAM-10k and natural quartz particles did not play a significant role on the kinetics of displacement of short polymer chains by the longer ones.

Nevertheless, we can notice that in both cases, simultaneous coadsorption (**Figure 2** and **Figure 3a**) or sequential adsorption (**Figure 3b** and **3c**), a small amount of shorter chains remain adsorbed on the surface. Two hypothesis can explained this observation. First this could reflect the occurrence of a few high energy adsorption sites on the natural quartz surface. This hypothesis is supported by the fact that two kind of adsorption sites are present on the natural quartz surface investigated in this study, i.e. silanol and aluminol groups. Indeed, we have previously shown that the presence of aluminol groups on natural quartz surface further increases the adsorption of acrylamide-based polymers.^{9, 33} This could explain the fact that some polymer chains still remain adsorbed on the particle surface despite the presence of polymer chains of higher molar mass. A second tentative explanation could be that despite the desorption of adsorbed chains by the longer ones, several shorter polymer chains can occupied the residual surface onto quartz particles and explain the observed results.

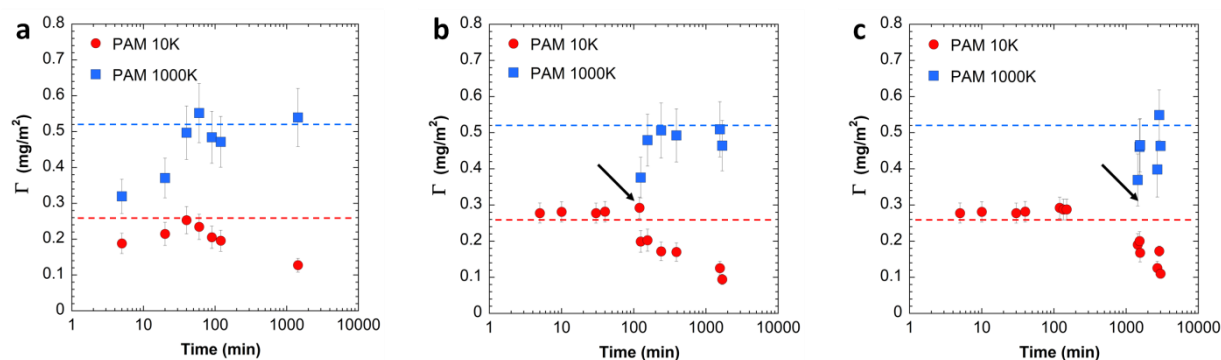


Figure 3: Competitive adsorption in time between PAM-10K and PAM-1000K at 0.2 g/L on natural quartz either by (a) coadsorption ($t=0$) or after a delay of (b) $t=2h$ and (c) $t=24h$. The dashed lines represent the maximum adsorption value, Γ_{max} , when the polymer is alone in solution. The arrow indicates the time (t_0) where the PAM-1000K is put in contact with the natural quartz/PAM-10K system. For the coadsorption, $t_0=0$ min.

CONCLUSION

In the present work, thanks to the coupling of size exclusion chromatography technique and the use of well-controlled polymers in size and distribution, we clarified the mechanism of competitive adsorption of PAM and HPAM on natural quartz. We evidenced that neutral and charged polyacrylamide exhibit the same behavior in presence of salts. Once the surface is mass saturated from the point of view of shorter polymer chains, the longer ones start desorbing the short ones. Besides, the contact time between the polymer and the surface did not seem to affect the mechanism involved. Even when the low molar mass chain polymers were added several hours before the higher ones, the outcome of competitive adsorption remained unchanged. However, we observed that even after a long equilibrium time, few polymer chains remained adsorbed onto the surface suggesting either the possible presence of anchoring sites with different adsorption energy or residual surface onto quartz particles. Moreover, by mixing different monodisperse polymers we were able to model a polydisperse system close to the real polydisperse macromolecules effectively encountered in industrial contexts.

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