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# Competitive adsorption of PAM and HPAM on Siliceous Material

H. Bessaies-Bey<sup>a,b,c,d,†</sup>, J. Fusier<sup>a,b,c,d,†</sup>, M. Hanafi<sup>a</sup>, S. Zhang<sup>a</sup>, M. Destarac<sup>c</sup>, S. Jouenne<sup>b,c,d</sup>, N.  
Passade-Boupat<sup>b,c,d</sup>, F. Lequeux<sup>a,b</sup>, J.-B. d'Espinose de Lacaillerie<sup>a,b</sup>, N. Sanson<sup>a,b\*</sup>

<sup>a</sup>Laboratoire Sciences et Ingénierie de la Matière Molle, ESPCI Paris, PSL  
University, Sorbonne Université, CNRS, F-75005 Paris.

<sup>b</sup>Laboratoire Physico-chimie des Interfaces Complexes, ESPCI Paris, 10 rue Vauquelin, F-75231  
Paris, France.

<sup>c</sup>TOTAL CSTJF, Avenue Larribau, Pau, France.

<sup>d</sup>Bâtiment CHEMSTARTUP, Route Départementale 817, 64170 Lacq, France.

<sup>e</sup>Université Paul Sabatier, Laboratoire des Interactions Moléculaires et de la Réactivité Chimique et  
Photochimique, UMR-CNRS 5623, Bât 2R1, 118 route de Narbonne, 31062 Toulouse, France.

\* Corresponding author.

E-mail address: nicolas.sanson@espci.fr (N. Sanson)

Present address: Soft Matter Science and Engineering laboratory, CNRS UMR 7615, ESPCI Paris,  
PSL University, Sorbonne Université, F-75005 Paris. Phone: +33 140 794 417

<sup>†</sup> H. B. and J. F. contributed equally to this work

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29 **ABSTRACT**

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

50

51

52 **INTRODUCTION**

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

58 Indeed, polymers, and in particular neutral (PAM) or partially hydrolyzed (HPAM)  
59 polyacrylamides are used in a wide range of industrial applications, such as water treatment  
60 by flocculation of particles<sup>1</sup>, soil stabilization,<sup>2, 3</sup> agriculture,<sup>4</sup> cement flow control,<sup>5-7</sup> and last

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

78 Concerning the competitive adsorption of polymers having different average molar  
79 masses, three main cases emerge from the literature: uncharged macromolecules<sup>10-15</sup> and  
80 polyelectrolytes in high<sup>16</sup> and low<sup>16,17</sup> salt content medium. Even if it is globally admitted that  
81 in the first two cases longer polymer chains preferentially adsorb to the substrate following  
82 entropic considerations<sup>18</sup> while in the third case it is the shorter polymer chains that are  
83 preferred because the system is then driven by the electrostatic energy balance, some  
84 questions remain:

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

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

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

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

115

## 116 **MATERIALS AND METHODS**

117 **Materials.** *Siliceous materials.* Crystallized natural quartz (99.5 % SiO<sub>2</sub>, 0.5 % Al<sub>2</sub>O<sub>3</sub>),  
118 named Sikaisol was acquired from Sika (Specific area  $S=0.56$  m<sup>2</sup>/g, determined by BET  
119 Nitrogen adsorption; bulk density  $\rho=2650$  kg/m<sup>3</sup>; mean particle diameter  $D=50$   $\mu$ m),

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

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

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

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

150 *Size Exclusion Chromatography (SEC) and data treatment.* Size exclusion chromatography  
151 was performed on a Malvern Viscotek TDA 302 system triple detector equipped with three  
152 OH-pak SB-806M HQ columns in series and a guard column. The mobile phase is an aqueous  
153 solution at 0.2 M NaNO<sub>3</sub> and the flow-rate is 0.7 mL/min. 100 µL of each sample is passed  
154 once in the set of columns before detection. The number- and weight average molar masses  
155 (respectively  $M_n$  and  $M_w$ ) and dispersity ( $D=M_w/M_n$ ) were derived from a universal calibration  
156 curve based on poly(ethylene oxide) standards from Malvern. Compared to TOC analysis,  
157 SEC experiments allows both to distinguish and quantify the polymers depending on their  
158 average molar mass.

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

166

167 **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

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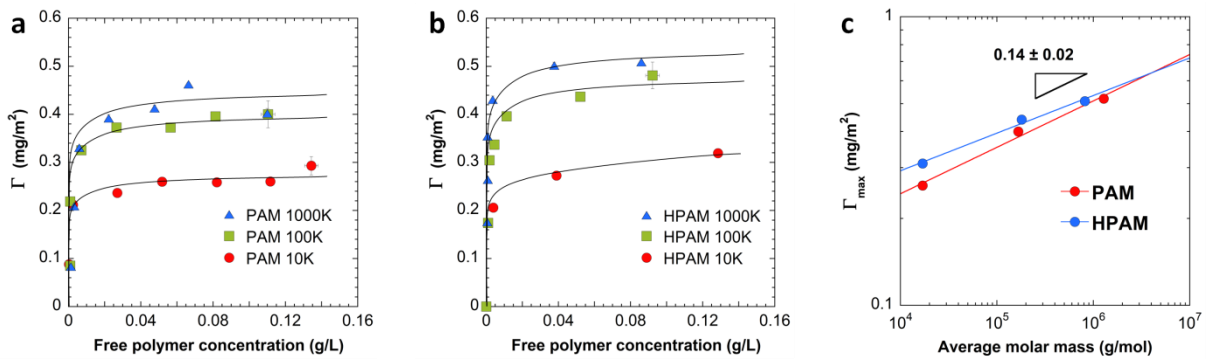
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## 172 **RESULTS AND DISCUSSION**

### 173 *Adsorption of PAM/HPAM on natural quartz*

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

184 be impacted by the physicochemical parameters of the polymer/particle system (pH,  
 185 temperature, ...) and notably the presence of electrolyte in solution which can decrease the  
 186 solubility of the polymer chains in solution and consequently increase the adsorbed amount.  
 187 In our two systems, PAM/H<sub>2</sub>O and HPAM/H<sub>2</sub>O/CaCl<sub>2</sub>, both polymer chains are in good  
 188 solvent as reported in the literature and in **Figure S2** (Supporting information) respectively.  
 189 At the pH of the suspensions (pH=6), both the HPAM and the silica surface groups are  
 190 negatively charged. However, during the adsorption of HPAM on natural quartz, the presence  
 191 of CaCl<sub>2</sub> screens the electrostatic repulsions between the HPAM and the silica surface. Hence,  
 192 HPAM in CaCl<sub>2</sub> solution behaved, as expected, similarly to PAM in pure water.  
 193 We moreover note that the maximum adsorption plateau,  $\Gamma_{\max}$ , increases when the average  
 194 molar mass of the polymer increases as shown in **Figure 1c**. Indeed, for both PAM/H<sub>2</sub>O and  
 195 HPAM/H<sub>2</sub>O/CaCl<sub>2</sub> systems, the maximum adsorption value varies as a function of molar  
 196 mass following a power law with a power exponent of 0.14. This value is consistent with the  
 197 reported values for uncharged macromolecules adsorbed on silica.<sup>14, 22, 25</sup>  
 198  
 199



**Figure 1:** Adsorption isotherms on natural quartz for (a) PAM in pure water and (b) HPAM in CaCl<sub>2</sub> solution (I=0.035 M). The lines are guides for the eyes (c) Maximum adsorption amount,  $\Gamma_{\max}$ , as a function of the average molar mass of acrylamide-based polymers.

200

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

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

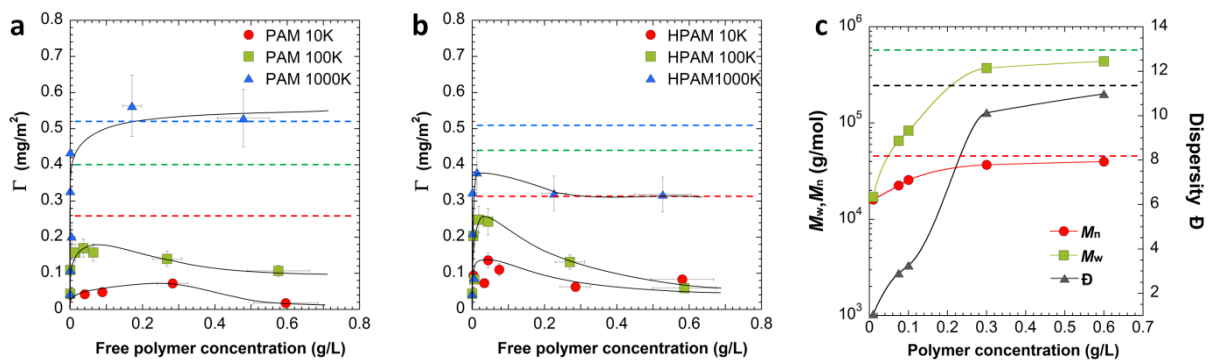


207 100K and HPAM-1000K, with the same weight fraction for each component. We chose to  
208 study the competitive adsorption of the three polymers by mass and not by number of chains  
209 for reasons of SEC sensitivity and viscosity of solution. Indeed conducting the study in terms  
210 of number of chains would result in a difference of two orders of magnitude between the mass  
211 concentrations between polymers having the lowest and the highest average molar mass.  
212 Knowing both  $M_n$  and  $M_w$  of each polymer, it is possible to compute the dispersity,  $\mathcal{D}$ , of the  
213 polymer mixtures. Dispersities of 11.4 and 7.9 were targeted, for PAM and HPAM mixture  
214 respectively, which is fairly representative of what can be used in industrial applications. The  
215 same adsorption protocol as for the individual polymer adsorption experiments was followed.  
216 Natural quartz particles are mixed with a solution of polymers mixture of varying  
217 concentrations for 24 hours at a solid to liquid ratio of 30 wt%. After centrifugation, the  
218 supernatant was then characterized with SEC. **Figure S3** in Supporting information shows the  
219 chromatogram of supernatant (i.e. non adsorbed polymer solution) obtained with a refractive  
220 index detector for different initial concentrations of PAM-10K, PAM-100K and PAM-1000K  
221 mixtures. The fitting of these chromatograms allows to determine the quantities of each mass  
222 distribution remaining in solution and consequently the quantities adsorbed onto the surface.  
223 Thereby the competitive adsorption of each polymer solutions containing three monodisperse  
224 polymers onto natural quartz particles can be plotted. For both polymer mixtures, PAM  
225 (**Figure 2a**) and HPAM (**Figure 2b**), the adsorption isotherm could be divided in two parts.  
226 First, at low concentrations of polymers, i.e. lower than 0.05 g/L, all species present in  
227 solution adsorbed on particles because there is enough space at the particles surface. This  
228 interpretation was supported by the chromatograms of the supernatant (**Figure S3** in  
229 Supporting information) where no polymers are detected in regards to the detection limits of  
230 the SEC technique. As illustrated in **Figure 2a** and **2b**, when increasing the polymer  
231 concentration, the adsorbed amount for the two polymers having the lowest average molar  
232 masses progressively decreased and tended toward zero while the polymer with the higher  
233 molar mass continued to adsorb onto particles until the saturation of the particles surface  
234 made it impossible to absorb more polymer chains onto it. In the case of the PAM mixture, we  
235 observed that the adsorption of the PAM-1000K reached the same adsorption value,  $\Gamma_{\max} \sim$   
236  $0.5 \text{ mg/m}^2$  as the one obtained by TOC for the polymer alone (**Figure 1a**). However, for the  
237 HPAM mixture it is worth noting that the adsorption of HPAM-1000K was significantly  
238 lower ( $0.3 \text{ mg/m}^2$ ) than the one of the polymer alone,  $\Gamma_{\max} \sim 0.5 \text{ mg/m}^2$ . A possible  
239 explanation would be that the ionic strength was too low to fully screen the particles surface  
240 charges as previously reported.<sup>9</sup> Then, electrostatic repulsion occurred either between the

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

248 Furthermore, it is also possible to calculate from these data the  $M_n$ ,  $M_w$  and  $\mathcal{D}$  values of the  
 249 supernatant composition for each concentration of polymer mixtures. To a certain extent,  
 250 these mixtures model the properties of a polymer with large dispersity during competitive  
 251 adsorption. The respective evolutions of each parameter are highlighted in **Figure 2c**. At low  
 252 surface coverage, the supernatant composition was very close from a pure solution of PAM-  
 253 10K in terms of  $M_n$  and  $M_w$ , with a dispersity close to 1. Then the dispersity and both the  
 254 number- and weight-average molar mass of the polymer mixture present in the supernatant  
 255 increased with concentration meaning that polymer chains having the highest molar mass start  
 256 to be present in the supernatant. This is due to the fact that the polymer chains with the  
 257 highest molar mass preferentially impact the weight-average molar mass of the polymer  
 258 mixture. Finally at higher dosage the macromolecular parameters ( $M_n$ ,  $M_w$  and  $\mathcal{D}$ ) tended  
 259 toward the properties of the initial mixtures (PAM-10K, PAM-100K and PAM-1000K equal  
 260 in weight proportions) illustrated by dashed lines in **Figure 2c**. This meant that the surface  
 261 was saturated and the polymer chains with different molar mass were present in the  
 262 supernatant. These observations were consistent with reported studies showing a modification  
 263 of the chromatogram of the supernatant after adsorption of polydisperse polymers on silica  
 264 particles.<sup>14, 26</sup>

265



**Figure 2:** Competitive adsorption on natural quartz of (a) PAM in pure water and (b) HPAM in CaCl<sub>2</sub>

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,  $\Gamma_{\max}$ , when the polymer is alone in solution. (c) Evolution of the average molar masses,  $M_w$  and  $M_n$ , and dispersity  $D$  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  $D$  of the initial polymer mixture.

266

267

### 268 *Adsorption-desorption kinetic aspects*

269 As observed in the previous section, the longer polymer chains, PAM-1000K or  
270 HPAM-1000K in electrolyte solution, adsorb preferentially on natural quartz to the detriment  
271 of polymer chains of molar masses lower by one or two orders magnitude. However, it should  
272 be kept in mind that literature results suggest that regardless of differences in molar masses,  
273 kinetics of adsorption/desorption can vary over orders of magnitude depending on the  
274 polymer structure, the substrate properties (chemical nature, porosity...) and the resulting  
275 adsorption driving force as well as the equilibrium time of the preadsorbed polymer chains.  
276 Indeed, Kawaguchi et al. studied by ellipsometry the competitive adsorption onto platinum  
277 plate between on the one hand 102 and 775 kg/mol, and on the other hand 422 and 775  
278 kg/mol polystyrene in theta conditions.<sup>27</sup> The authors reported that the kinetics of  
279 displacement by 775 kg/mol polymer chains of 442 kg/mol polystyrene is slower than for 102  
280 kg/mol. Then, they noted that the displacement of shorter polymer chains is complete after  
281 20h. The same observations have been made by Fu et al. for the competitive adsorption of  
282 poly(ethylene oxide) chains having different molar masses on glass.<sup>12, 28</sup> However, they  
283 noticed that short PEO chains become more difficult to displace from the surface when their  
284 contact time with the interface or the relative molar mass of the preadsorbed polymer chains is  
285 increased.<sup>29</sup> Conversely, rapid and total displacement, on the order of several hours, have been  
286 also observed in the literature for polystyrene/silica system.<sup>14, 30</sup> In summary, we can conclude  
287 from the literature that the kinetics of displacement of adsorbed polymer chains is highly  
288 system dependent.

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

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

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

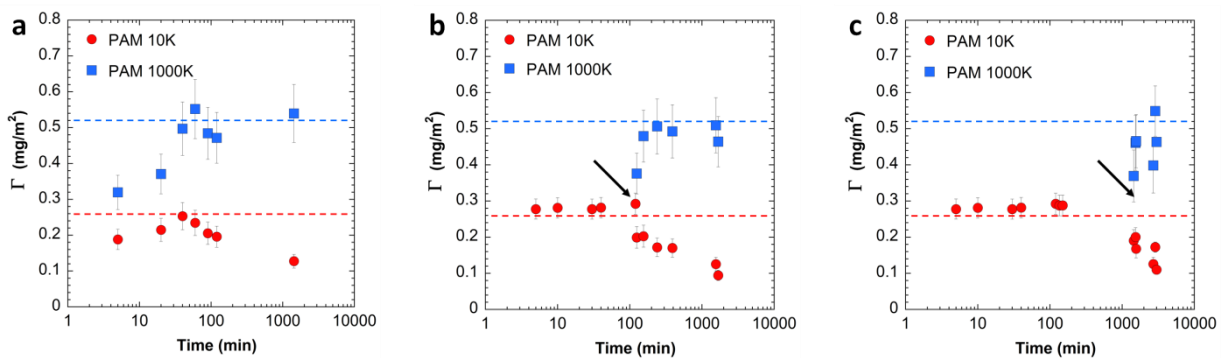
328 PAM-1000K is added to the sample, PAM-10K started desorbing whereas adsorption of  
 329 PAM-1000K increased which means that the contact time between PAM-10k and natural  
 330 quartz particles did not play a significant role on the kinetics of displacement of short polymer  
 331 chains by the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

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

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**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,  $\Gamma_{max}$ , 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.

348

349 **CONCLUSION**

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

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