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# Mesoporous Silica Colloids: Wetting, Surface Diffusion and Cationic Surfactant Adsorption

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## ABSTRACT

We have investigated the wetting and surface diffusion of mesoporous colloidal silica particles at the water surface; and the adsorption of cationic cetyltrimethylammonium (CTA<sup>+</sup>) surfactant on these particles. Porous silica colloids diffuse at the surface of water and in the volume, interacting with cationic surfactants that can adsorb inside the pores of the particles. We observed that surfactant adsorption on mesoporous silica depends dramatically not only on the particle pore size but also on specific counterion effects. We measured striking differences both on a macroscopic property of the interface, i.e. surface tension, and also at a single particle level by evaluating the translational diffusion of partially wetted particles at the fluid interface. We varied the pore size from 2 to 7 nm and explored the effects of ions owing different hydration number and kosmotropic/chaotropic character. At concentrations lower than the critical micellar concentration, we evidence that cationic surfactants adsorb on silica as surface micelles and surfactant adsorption inside the pores occurs only if the pore diameter is larger than the size of surface micelles. With a view to understand the surprising different adsorption behavior of CTA<sup>+</sup>OH<sup>-</sup> and CTA<sup>+</sup>Br<sup>-</sup> on porous silica particles, we investigated the effect of counterions on the surfactant adsorption on porous silica colloids by tuning the pH and the counterion properties.

## INTRODUCTION

Cationic surfactants are widely used in many industrial and fundamental research fields ranging from cosmetics, fabrics, nanoparticles synthesis, DNA folding, self-assembly and mesoporous material fabrication.<sup>1,2</sup> Besides these applications, the fate of cationic surfactants and the resulting waste in water is an important issue, since cationic surfactant contamination of water represents a real environmental problem.<sup>3</sup> Current methods to remove surfactants from water involve the use of organophilic clays, flocculants or carbon beds.<sup>4-8</sup> In many separation methods, surfactant removal by adsorption onto solid substrates is required. Hence, both large surface areas and an effective attraction between the surfactant and the solid are necessary to drive soluble surfactants adsorption on the solid boundaries.

Adsorption of cationic surfactants on planar solid surfaces has been investigated for several surfactant-substrate systems. For cetyltrimethylammonium (CTA<sup>+</sup>) surfactants on silica surfaces, different adsorption regimes are found as a function of the surfactant concentration, surface charge and

39 hydrophobic interaction.<sup>9,10</sup> At low concentrations, surfactant may adsorb onto the silica surface as a  
40 monolayer, as defective bilayers or as surface micelles.<sup>11,12</sup> These micellar structures are flattened by the  
41 surface and possess a thickness of 3.5 nm and a lateral size of 9 nm.<sup>10</sup> Upon increasing the concentration,  
42 bilayers may form due to the interaction between the hydrophobic chains. It is important to notice that the  
43 interfacial self-assembled structures usually appear at a concentration lower than the usual critical  
44 micellar concentration (CMC) in the volume.<sup>11</sup> For CTA<sup>+</sup> surfactants at concentrations  $C$  lower but close  
45 to CMC, surface excess concentrations  $\Gamma$  between  $\approx 1$  and  $\approx 2$  mg/m<sup>2</sup> have been reported.<sup>11,13–15</sup>

46 As pointed out before, solid substrates with large specific areas are required for adsorption in order to  
47 separate surfactants from clean water. In this context, porous particles are ideal candidates given the large  
48 surface/volume ratio, which can be tuned by the pore size and volume fraction.<sup>16,17</sup> However, adsorption  
49 inside a pore strongly differs from the adsorption on a planar interface. Pore size and morphology affect  
50 the adsorption process, which depends on differences in pressure and physicochemical properties inside  
51 and outside the pores.<sup>18</sup>

52 Non-ionic surfactants adsorption onto mesoporous silica particles has been widely investigated by  
53 Findenegg and coworkers.<sup>19–22</sup> Bilayers formation and other structures inside the pores has been reported.  
54 Very few experimental investigations can be found in the literature for the adsorption of cationic  
55 surfactants onto mesoporous silica. A small angle neutron scattering investigation reported some  
56 preliminary experiments for 8 nm pore size mesoporous silica at pH=9 where an increase of cationic  
57 surfactant adsorption occurs if the ionic strength is increased.<sup>23</sup> Cationic surfactant interacting with silica  
58 nanoparticles have been also recently investigated.<sup>1,24–26</sup>

59 Here, we have investigated the wetting and diffusion of porous silica colloids, and the adsorption of  
60 cationic surfactants on porous colloidal particles. Porous colloids of different pore sizes are deposited  
61 both in the bulk and at the interface. By varying pore size, surfactant concentration and investigating  
62 counterion effects we aim at controlling CTA<sup>+</sup> cationic surfactant adsorption. These results could be used  
63 in order to develop a strategy to clean the surface and the volume of water with micron sized particles,  
64 which are small enough to perform Brownian motion and rapidly diffuse at the interface (and in the  
65 volume) but also large enough to slowly sediment. These porous colloids may be ideal candidates for an  
66 efficient removal of surfactants at low concentrations and present the advantage to be easily removed  
67 after decontamination by sedimentation or flotation. Note that larger particles are difficult to adsorb at the  
68 interface and may sediment very fast; whilst nanoparticles may remain dispersed in water due to the  
69 strong Brownian motion and cannot be separated by gravity or adsorption on bubbles as in flotation.

70

71

## 72 MATERIALS AND METHODS

73 *Materials.* All chemicals, except for the in-house synthesized colloids, were purchased from Sigma  
74 Aldrich and used without further purification. Two surfactants were investigated:  
75 cetyltrimethylammonium bromide CTA<sup>+</sup>Br<sup>-</sup> (CAS 57-09-0, molecular weight  $M_w = 364.45$  g/mol) and  
76 cetyltrimethylammonium hydroxide CTA<sup>+</sup>OH<sup>-</sup> (10 wt.% in H<sub>2</sub>O, CAS 505-86-2,  $M_w = 301.55$  g/mol).  
77 Three different batches of porous silica particles were also employed. The first two consist of spherical  
78 mesoporous silica colloids (CAS 7631-86-9) with an average radius  $\bar{R} = 1.23 \pm 0.10$   $\mu\text{m}$  (measured by  
79 scanning electron microscopy, SEM) and nominal pore diameter  $d = 2$  nm and  $d = 4$  nm and a specific  
80 area  $S_A = 1000 \pm 100$  m<sup>2</sup>/g for  $d = 2$  nm and  $S_A = 350 \pm 50$  m<sup>2</sup>/g for  $d = 4$  nm. A third batch of non-  
81 spherical mesoporous silica particles was synthesized in the laboratory. These last particles are currently

82 called Santa Barbara amorphous-15 silica (SBA-15). The average pore diameter is larger than the  
83 previous ones:  $d = 7$  nm measured by volumetric nitrogen sorption isotherms. Stable particle dispersions  
84 were obtained by sonication of 1.2 mg/mL dispersions in an ultrasound bath for one hour. We measured  
85 the Feret diameter<sup>27</sup> of these particles by scanning electron microscopy, which leads to an equivalent  
86 radius  $\bar{R} = 1.96 \pm 0.97$   $\mu\text{m}$  (*i.e.* half of the Feret diameter). The pores are about a micron long and  
87 connected via mesoporous walls. A total specific area of  $750 \pm 50$   $\text{m}^2/\text{g}$  was evaluated by Brunauer-  
88 Emmett-Teller (BET) method. Pore size distributions were determined by the (Barrett, Joyner, Halend)  
89 BJH method.<sup>28</sup> Mesoporous walls contribute significantly to the total specific area in terms of  
90 microporosity (size  $< 1\text{-}2$  nm). We evaluate a total specific area  $S_A = 225 \pm 25$   $\text{m}^2/\text{g}$  for the  $d = 7$  nm pore  
91 size (See Figure S1 in Supporting Information, SI).

92 NaOH, NaBr, NaCl salts were used as received. Fresh Milli-Q water was used throughout this work.  
93 Experiments were carried out at room temperature  $T = 22$   $^\circ\text{C}$ .

94 *Surface tension and sessile drop contact angle.* Surface tension was used to measure surfactant adsorption  
95 on porous particles. All measurements were performed in a 9 cm diameter polystyrene Petri dish  
96 containing a volume  $V = 35$  mL of surfactant solutions at different concentrations  $C$  and a fixed mass (1.2  
97 mg) of porous particles. For planar aqueous surfaces contained in a Petri dish, surface tension was  
98 measured by the Wilhelmy plate method (KSV NIMA, Biolin Scientific) using a filter paper plate. In order  
99 to evaluate the interfacial tensions of the silica-surfactant solutions-gas systems, we also measured the  
100 surface tension of aqueous solutions and the advancing contact angle  $\theta$  of sessile drops by a profile  
101 analysis tensiometer (PAT, Sinterface, Germany). A typical volume of the aqueous drop in PAT  
102 experiments is  $15$   $\text{mm}^3$ . Series of experiments were repeated at least three times and show a good  
103 reproducibility. For interfacial tension measurements, the standard deviations of the data obtained in  
104 different experimental campaigns lay between 1 and 3 mN/m, which can be related to the experimental  
105 protocols: particle deposition, aging of particle dispersions and surfactant solutions (*i.e.* maximum 5  
106 days).

107 *Particle dispersion deposition.* The final chosen method adopted to deposit porous particles at the  
108 interface is to drop 1 mL of a 1.2 mg/mL particle suspension on a tilted glass slide placed at the air-water  
109 interface and let it slip.<sup>29</sup> Particle density at the interface can be calculated by counting the particle  
110 number using optical microscopy. For all porous particle systems, we evaluated an average surface  
111 coverage of  $6.5 \pm 2$  particles per  $\text{mm}^2$  (if 1.2 mg of silica porous particles are added in the Petri dish). From  
112 the latter value, one can estimate the ratio between the total number of particles  $N_{tot}$  and the ones trapped  
113 at the surface  $N_s$ :  $N_{tot}/N_s \approx 10^6$ , which is very high, meaning that only few particles stay at the interface.  
114 We have put many efforts to find protocols to increase the number of particles remaining at the air-  
115 aqueous solution interface and try several methods. However, protocols involving spraying or the use of  
116 additional volatile solvents were discarded since they do not allow the control of the particles numbers or  
117 introduce additional sources of contamination and uncertainties. It is important to note that even if  $N_{tot}/N_s$   
118  $\approx 10^6$ , the amount of particles at the interface is non-negligible for the adsorption of soluble surfactants,  
119 which accumulate preferentially at the interface but they are also present in the bulk, see Figure S2 in SI.

120 *Particle contact angle by gel trapping.* We measured the particle contact angle of porous silica colloids  
121 using a gel trapping technique.<sup>30</sup> Few microliters of a diluted solution of particles were added to a gelled  
122 solution of Phytigel (CAS 71010-52-1, Sigma Aldrich) in a small container. After heating up the gel to  
123 the liquid state, the particles get trapped at the interface. Going back to the room temperature, a UV-glue  
124 was used to transfer the particles from the gel to the glue substrate. The contact angle was measured using

125 scanning electron microscopy images of the transferred particles on the solidified glue at their  
126 complementary contact angle positions.

127 *Particle tracking.* Bright field optical microscopy was used for particle tracking. Experiments were  
128 performed in an upright Leica optical microscope mounted on an anti-vibration table. Images of isolated  
129 particles were recorded using a CMOS camera (Orca Flash 4.0, Hamamatsu) at rates of 80 or 100 frames  
130 per second using objectives of different magnifications ( $\times 63$  and  $\times 100$ ). Tracking of the particle location  
131 was done by an *IDL* routine or by using an image correlation-based approach (“Stat Tracker St.  
132 Andrews”) implemented in Labview (National Instruments).

133 *Zeta potential and pH measurements.* We measured the zeta potential  $\zeta$  (Zetasizer Nano ZS, Malvern  
134 Instruments) and the pH of the particle dispersions in pure water or in the presence of surfactants. For  
135 porous silica colloids dispersions, a pH = 6.4 was always measured in pure water.

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## 138 RESULTS AND DISCUSSION

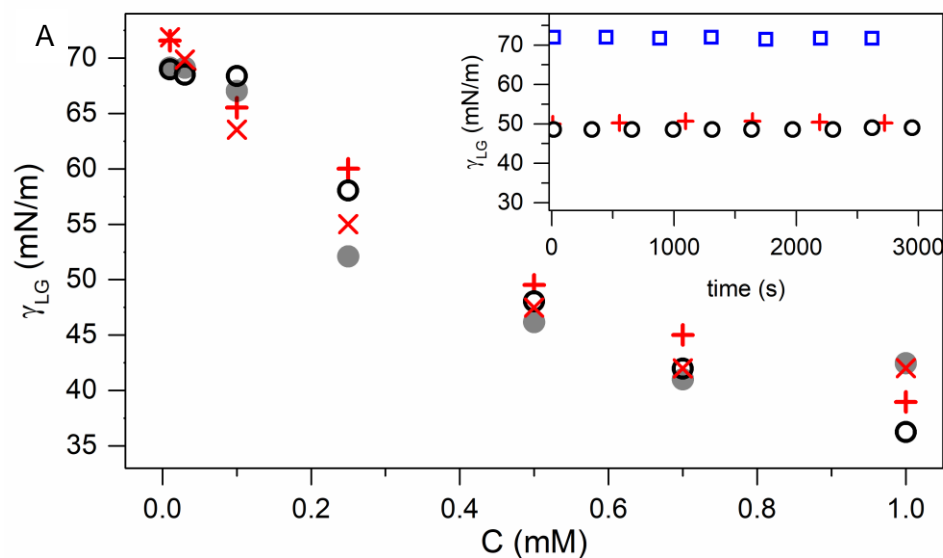
### 139 Interfacial tensions of $\text{CTA}^+\text{Br}^-$ and $\text{CTA}^+\text{OH}^-$ at the liquid-gas and solid-liquid 140 interfaces

141 We started characterizing the adsorption of  $\text{CTA}^+$  surfactants on non-porous silica by evaluating the  
142 interfacial tension between silica and the aqueous surfactant solutions,  $\gamma_{\text{SL}}$ . Young equation for a sessile  
143 drop of aqueous surfactant solutions on a silica substrate in air reads:

$$144 \gamma_{\text{SG}} = \gamma_{\text{SL}} + \gamma_{\text{LG}} \cos \theta, \quad (1)$$

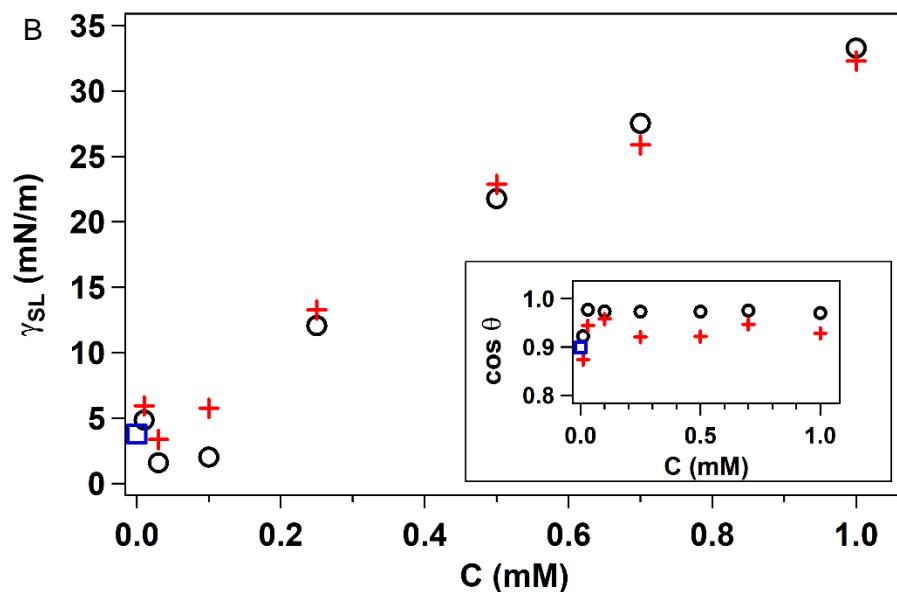
145 where the subscripts S, L and G represent solid, liquid and gas respectively. One can evaluate  $\gamma_{\text{SL}}$   
146 measuring the interfacial tension  $\gamma_{\text{LG}}$ , the sessile drop static contact angle  $\theta$  and assuming that  $\gamma_{\text{SG}}$  is a  
147 constant (and does not vary with the surfactant concentration). Surface tension at the air-aqueous solution  
148 interface  $\gamma_{\text{LG}}$  for  $\text{CTA}^+\text{Br}^-$  and  $\text{CTA}^+\text{OH}^-$  surfactant was measured by the Wilhelmy plate technique and  
149 pendant drop tensiometry. The two methods lead to very similar results as shown for a series of  
150 experiments in Figure 1A. The evolution of  $\gamma_{\text{LG}}$  as a function of the surfactant concentration  $C$  for both  
151 surfactants shows no significant difference. In addition,  $\gamma_{\text{LG}}$  values are stable and do not change in a  
152 typical experimental time range of 3000 s (inset of Figure 1A). Sessile drops made with surfactants  
153 solutions were deposited on clean glass slides and their contact angles  $\theta$  were also evaluated by imaging  
154 the drop profile (and the  $\cos \theta$  is plotted in the inset of Figure 1B for a series of experiment).<sup>31</sup> Hence,  $\gamma_{\text{SL}}$   
155 can be calculated from eq. 1 with  $\gamma_{\text{SG}} = 68.5$  mN/m as reported by Binks et al.<sup>32</sup> for silica surfaces  
156 showing water contact angle similar to our experiments. Unexpectedly the silica-aqueous solution  
157 interfacial tension  $\gamma_{\text{SL}}$  shows a non-monotonic behavior if the surfactant concentration is increased.<sup>33,34</sup> For  
158  $C \geq 0.1$  mM,  $\gamma_{\text{SL}}$  increases if  $C$  increases, instead of decreasing as  $\gamma_{\text{LG}}$ . Hence, the Gibbs adsorption valid  
159 for ideal dilute solutions for  $C < \text{CMC}$  ( $\approx 0.8\text{-}0.9$  mM)<sup>10,35</sup> can be applied only for the air-liquid interface,  
160 where a surface concentration  $\Gamma \approx 1$  mg/m<sup>2</sup> at the CMC can be evaluated.<sup>36</sup> For  $C < 0.1$  mM at the solid-  
161 liquid interface, one could also observe a tiny decrease of the interfacial tension which could correspond  
162 to an increasing accumulation of non-interacting surfactants at the solid-liquid interface.<sup>37</sup> However for  $C$   
163  $\geq 0.1$  mM, the increase of  $\gamma_{\text{SL}}$  points to the formation of self-assembled structures as bilayers<sup>38</sup> or surface  
164 micelles, which form because of the hydrophobic interactions between surfactant tails. Note that the

165 concentration at which the interfacial tension  $\gamma_{SL}$  increases is about 10 times lower than the CMC.<sup>10</sup> An  
 166 increase of the interfacial tension  $\gamma_{SL}$  reveals that the surface is increasing in hydrophobicity due to the  
 167 presence of hydrophobic surfactant groups. As already pointed out in the Introduction, the presence of  
 168 bilayers or surface micelles on planar silica surfaces has been widely reported but to the best of our  
 169 knowledge was never connected to a minimum in the interfacial tension  $\gamma_{SL}$ .



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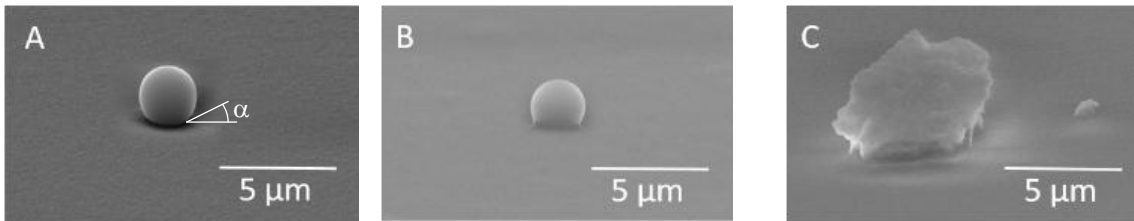
174 Figure 1. (A) Liquid-gas interfacial tension of  $\text{CTA}^+\text{Br}^-$  (+,  $\square$ ) and  $\text{CTA}^+\text{OH}^-$  (-,  $\circ$ ) as a function of the  
 175 concentration obtained by pendant drop tensiometry (+, -) and by Wilhelmy plate method ( $\square$ ,  $\circ$ ); inset: interfacial  
 176 tension as a function of time for pure water ( $\nabla$ ) and  $\text{CTA}^+\text{Br}^-$  (+) and  $\text{CTA}^+\text{OH}^-$  (-) at  $C = 0.5$  mM. (B) Solid-liquid

177 interfacial tension  $\text{CTA}^+\text{Br}^- (+)$  and  $\text{CTA}^+\text{OH}^- (-)$  evaluated by the Young equation and advancing contact angle  
 178 measurement of sessile drops on silica (inset). Data for pure water ( $\nabla$ ) are also shown.

179

## 180 Porous particles at the interface

181 The contact angle of porous particles at the gas-liquid interface was measured by a gel trapping method  
 182 (see Materials and Methods). Figure 2 shows images of particles at their complementary contact angle  
 183 positions. We have also observed some crater shape footprints on the solidified substrate, which  
 184 correspond to particles possessing very low contact angles. For spherical porous particle, we measured  
 185 particle contact angle  $\alpha = 47^\circ \pm 6^\circ$  for  $d = 2$  nm and  $\alpha = 52^\circ \pm 14^\circ$  for  $d = 4$  nm (Figure 2A and B). Non-  
 186 spherical porous particles show also a finite immersion at the air-water interface that is comparable to the  
 187 contact angle observed for the spherical porous particles.



192 Figure 2. SEM images of gel trapped  $\bar{R} = 1.23$   $\mu\text{m}$  spherical mesoporous silica colloids  $d = 2$  nm (A) and  $d = 4$  nm  
 193 (B); and a non-spherical silica particle of equivalent radius  $\bar{R} = 1.96$   $\mu\text{m}$  (diameter = 3.92  $\mu\text{m}$ ) and  $d = 7$  nm (C).

194

195 It is important to notice that the measured contact angle of a sessile water drop on silica,  $\theta \approx 26^\circ$ , is  
 196 significantly lower than the contact angles of porous silica particles shown in Figure 2:  $\alpha > \theta$ . In order to  
 197 explain this result, we start discussing the partial wetting state of porous particles and compare it to the  
 198 reference case of a bare solid spherical particle, see Figure 3. For a bare particle, the equilibrium of  
 199 interfacial tensions leads to the Young equation (see equation 1). For smooth and homogenous surfaces,  
 200 the bare solid micron-sized particle contact angle should be identical to the contact angle of a sessile  
 201 liquid drop on a flat solid substrate:  $\alpha_B = \theta$ .<sup>39</sup> In the framework of the Cassie-Baxter model valid for  
 202 composite interfaces, two different scenario can be considered for porous particles at the interface.

203 In the first case, we consider that the pores of the particles are completely filled by the liquid. In this case,  
 204 the particle interfacial tensions  $\gamma_{\text{SG}}$  and  $\gamma_{\text{SL}}$  change if compared to the bare particle case. The interfacial  
 205 tension of the particle exposed to the liquid will be reduced from  $\gamma_{\text{SL}}$  to  $f\gamma_{\text{SL}}$ , where  $f$  is the solid area  
 206 fraction on the particle surface, see Figure 3. The particle surface exposed to the gas phase can be  
 207 regarded as a composite interface made of solid and liquid.<sup>39</sup> The resulting equilibrium of interfacial  
 208 tensions reads:

$$209 \quad f\gamma_{\text{SG}} + (1-f)\gamma_{\text{LG}} = f\gamma_{\text{SL}} + \gamma_{\text{LG}} \cos \alpha. \quad (2)$$

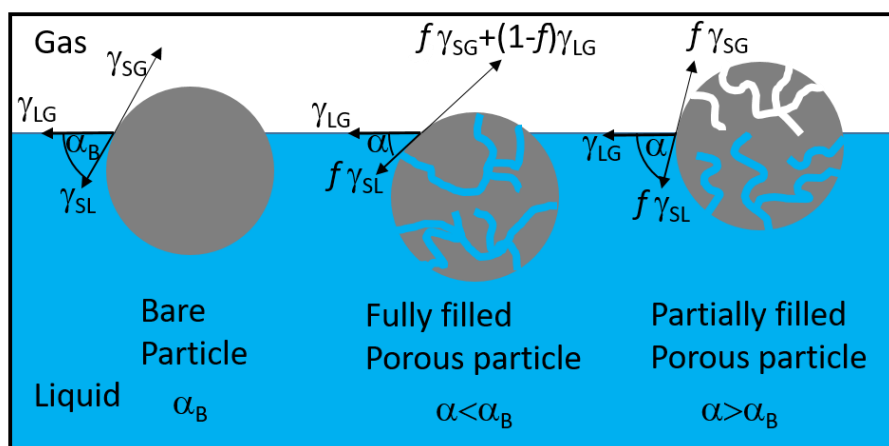
210 Except for  $f$ , all the other variables in equation 2 are measured. In pure water,  $\gamma_{\text{SG}} = 68.5$  mN/m,  $\gamma_{\text{LG}} =$   
 211 72.5 mN/m and  $\gamma_{\text{SL}} = 4$  mN/m (Figure 1). According to equation 2,  $\alpha$  decreases if  $f$  decreases and the  
 212 Young equation is recovered if  $f=1$ . Actually for porous particles with pores completely filled by the  
 213 liquid, the particle contact angle  $\alpha$  is expected to be low,  $\alpha < \theta$ , which explains the observation of crater  
 214 footprints in SEM images and the large number of particles in the volume with respect to the particles  
 215 present at the interface (see Particle dispersion deposition section). Note also that the interfacial energy

216 gain associated to the adsorption of a bare particle at the interface  $\gamma_{LG}A_0$  due to the removal of a bare fluid  
 217 interface area ( $A_0 = \pi R^2 \sin^2 \alpha$ ) is strongly reduced for a porous particle given the presence of liquid inside  
 218 the particle.<sup>39</sup>

219 A second scenario can be considered to explain the results shown in Figure 2, where  $\alpha > \theta = \alpha_B$  (Figure  
 220 3). In this case, the liquid is not present on the porous particle surface exposed to the gas phase. Hence,  
 221 the external surface can be regarded as a composite surface made of solid and air, and the interfacial  
 222 tension of this surface becomes  $f\gamma_{SG}$ . The resulting equilibrium of interfacial tensions reads:

$$223 \quad f\gamma_{SG} = f\gamma_{SL} + \gamma_{LG} \cos \alpha. \quad (3)$$

224 In this second case, the contact angle of a porous particle can be higher than the contact angle of an  
 225 equivalent bare particles. Equation 3 can be rewritten in the form  $\cos \alpha = \frac{f(\gamma_{SG} - \gamma_{SL})}{\gamma_{LG}} = f \cos \theta$  (see  
 226 equation 1), which leads to solid area fraction  $f = 0.76$  for 2 nm and  $f = 0.68$  for 4 nm pore size porous  
 227 particles.



228  
 229 Figure 3. Sketches of a bare non-porous particle (left), a porous particle with pores completely filled by the liquid  
 230 (center) and a porous particle with pores partially filled by the liquid (right) in mechanical equilibrium at the gas-  
 231 liquid interface.

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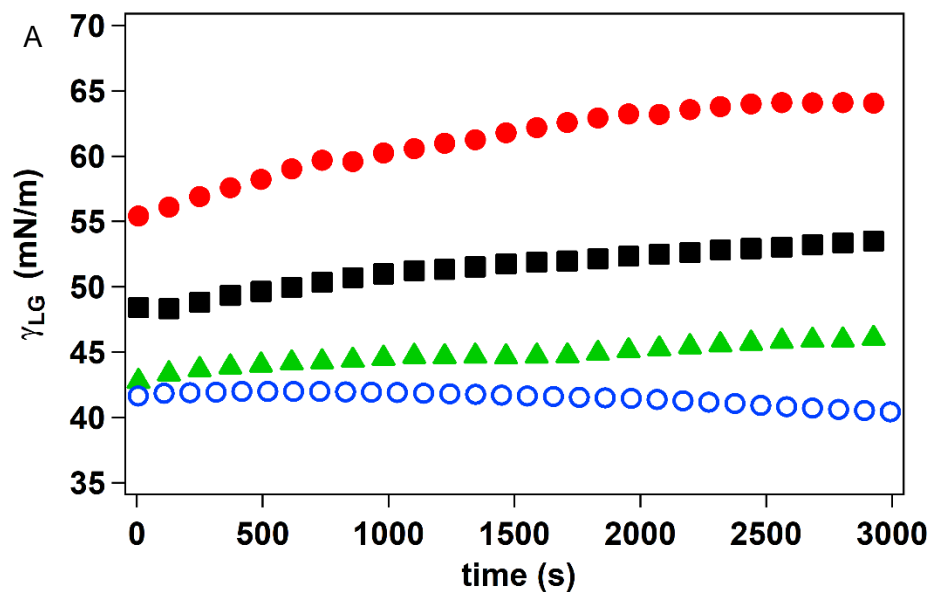
### 233 **Influence of particle pore size on surfactant adsorption**

234 In order to measure the surfactant adsorption on porous silica colloids we performed surface tension  
 235 experiments using a Wilhelmy plate apparatus. Starting from a stable interfacial tension measurement at a  
 236 given surfactant concentration  $C$ , porous colloids are deposited at the air-aqueous solution interface via a  
 237 tilted glass slide. Note that the addition of few porous colloids (1.2 g in 35 mL water) in absence of  
 238 surfactants does not affect the interfacial tension  $\gamma_{LG}$ . As a consequence of the addition of mesoporous  
 239 particles, we record an increase of the liquid-gas interfacial tension connected to a surfactant removal  
 240 from the aqueous solution due to the adsorption on porous silica colloids.

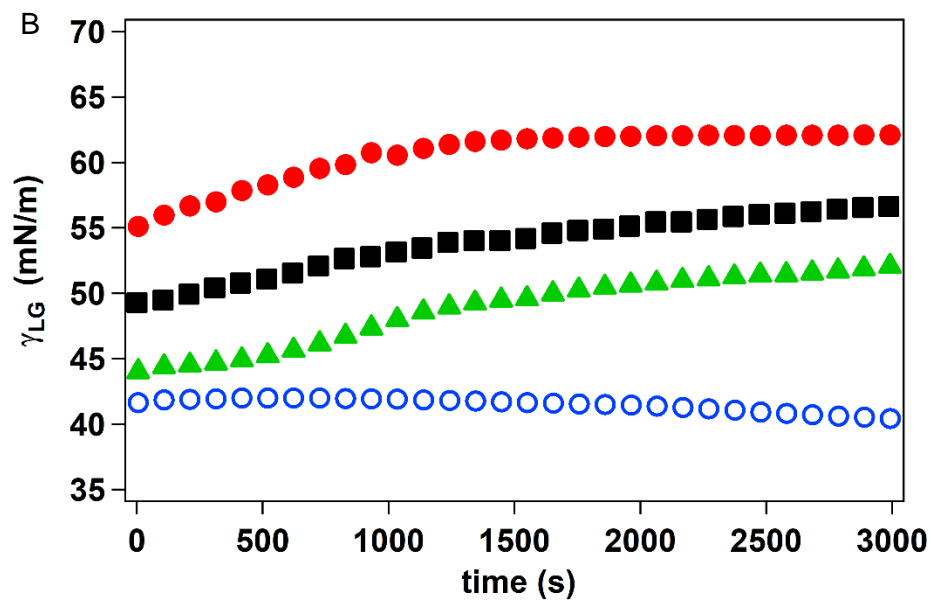
241 In Figure 4 we show a series of surface tension experiments of  $\text{CTA}^+\text{Br}^-$  and  $\text{CTA}^+\text{OH}^-$  solutions at  
 242 different surfactant concentrations in the presence of a fixed number of porous silica particles of 4 and 7  
 243 nm pore diameters  $d$ . For  $\text{CTA}^+\text{OH}^-$  in the presence of the  $d = 4$  nm (Figure 4A) and 7 nm (Figure 4B)  
 244 porous silica particles, we measured a significant increase in the surface tension, which is a clear evidence



245 of surfactant removal from the aqueous solution. When adding  $d = 4$  nm porous silica colloids, the  
246 interfacial tension increases by 8 mN/m, 5 mN/m and 4 mN/m for 0.25 mM, 0.5 mM and 0.7 mM  
247 respectively. As for the  $d = 7$  nm porous silica colloids, the surface tension increases by 12 mN/m, 9  
248 mN/m and 7 mN/m for 0.25 mM, 0.5 mM and 0.7 mM respectively. Surprisingly, no apparent increase in  
249 the surface tension with  $\text{CTA}^+\text{Br}^-$  was observed, which will be further analyzed and discussed in the  
250 following sections. No adsorption for both  $\text{CTA}^+\text{Br}^-$  and  $\text{CTA}^+\text{OH}^-$  was also observed for  $d = 2$  nm  
251 porous silica colloids, see Figure 5. Surface tension measurements showed no variation before and after  
252 adding the  $d = 2$  nm porous particles (Figure 5), leading to the conclusion that a pore size of 2 nm is too  
253 small for  $\text{CTA}^+$  cationic surfactant adsorption. This result agrees with the increase of  $\gamma_{\text{SL}}$  shown in Figure  
254 1B and connected to the formation of surface micellar structures at concentrations much lower than the  
255 CMC. Surfactants may adsorb inside the pores as micellar structures and not as single molecules. The size  
256 of micelles in the bulk<sup>10</sup> (for  $C \approx \text{CMC}$ ) is between 2.6 and 4.7 nm; and for  $C < \text{CMC}$  the thickness of  
257 surface micelles is about 3.5 nm for  $\text{CTA}^+\text{Br}^-$ . Hence, these dimensions are always larger than the size of  
258 2 nm and explain why adsorption is not observed in  $d = 2$  nm porous particles.



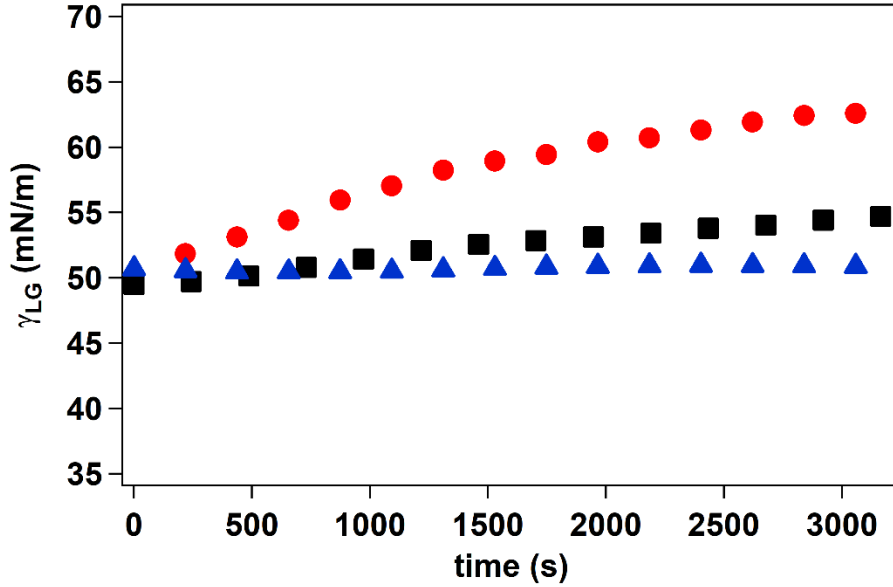
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260

261 Figure 4. Liquid-gas interfacial tension as a function of time after the deposition of  $d = 4$  nm porous silica particles  
 262 (A) and  $d = 7$  nm particles (B) at different  $\text{CTA}^+\text{OH}^-$  surfactant concentrations:  $C = 0.25$  mM ( $\circ$ ),  $0.5$  mM ( $\triangle$ ),  $0.7$   
 263 mM ( $\nabla$ ); and  $\text{CTA}^+\text{Br}^-$  concentration  $C = 0.7$  mM ( $\square$ ).  $1.2$  g of particles were added in  $35$  mL solution.

264



265

266 Figure 5. Liquid-gas interfacial tension as a function of time for CTA<sup>+</sup>OH<sup>-</sup> at  $C = 0.5$  mM in the presence of  $d = 7$   
 267 nm (●),  $d = 4$  nm (■) and  $d = 2$  nm (▲) porous silica particles (1.2 g of particles in 35 mL).

268

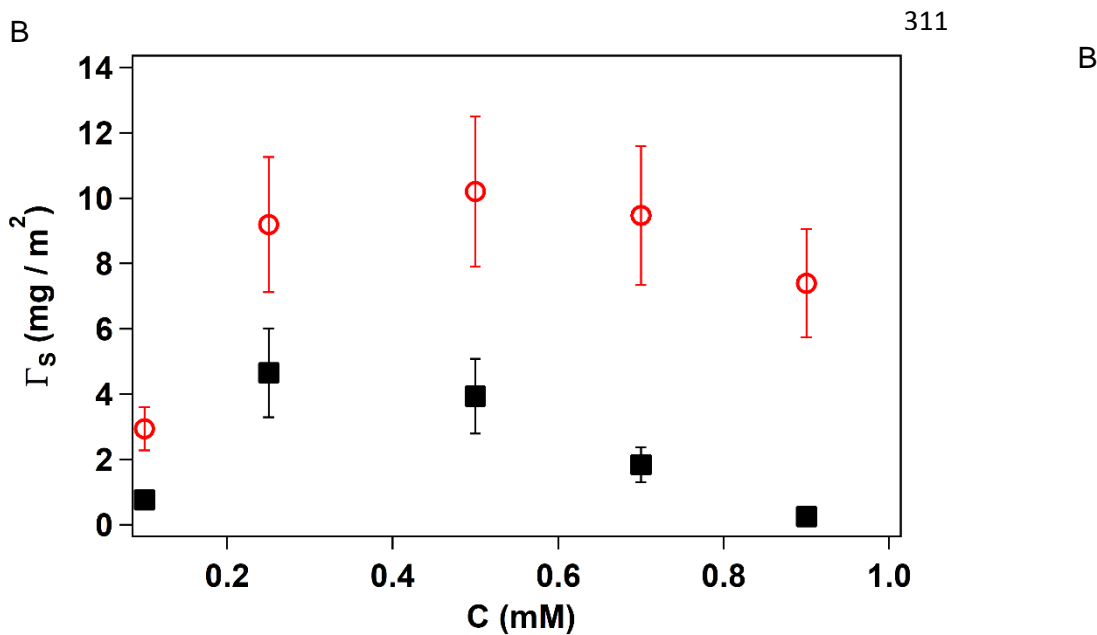
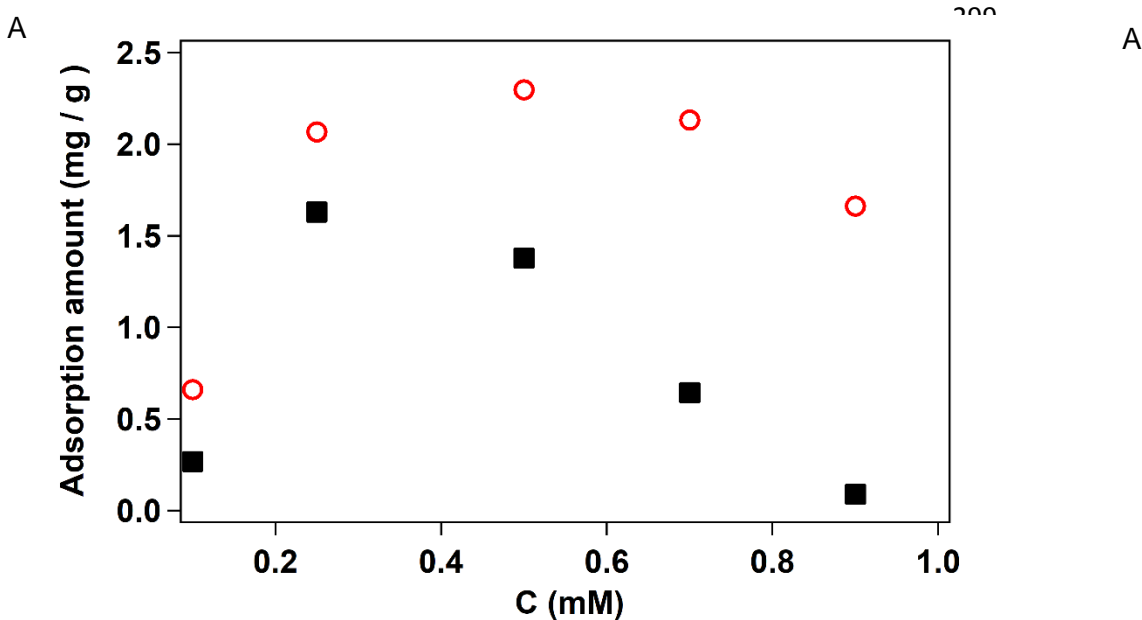
269 Knowing the initial CTA<sup>+</sup>OH<sup>-</sup> surfactant concentration  $C$  and the interfacial tension  $\gamma_{LG}$  after adsorption  
 270 (at time  $t = 3000$  s in Figure 4 and 5), we can extract the final surfactant concentration  $C_f$  in the solution  
 271 using the  $\gamma_{LG}$  vs  $C$  data (eventually interpolated) shown in Figure 1A. Hence, we can calculate the total  
 272 mass of surfactant removed in the  $V = 35$  mL solution as  $(C - C_f)V$ . In Figure 6A, the adsorption amount  
 273 (which is the mass of surfactants divided by the mass of porous particles) is plotted as a function of the  
 274 initial surfactant concentration. For  $d = 7$  nm porous silica particles, the adsorption amount increases up  
 275 to 2 mg/g at intermediate concentrations. For  $d = 4$  nm porous silica particles instead a maximum in the  
 276 adsorption amount is clearly observed at  $C = 0.25$  mM, above which the adsorption amount decreases.  
 277 Knowing the mass  $m$  ( $=1.2$  mg) of the porous particles and their specific areas  $S_A$  (see Materials and  
 278 Methods), we can also calculate the surfactant surface concentration  $\Gamma_S$  on the total silica area ( $= mS_A$ ):

$$279 \quad \Gamma_S = \frac{(C - C_f)V}{m S_A} \quad (4)$$

280 Figure 6B shows  $\Gamma_S$  as a function of CTA<sup>+</sup>OH<sup>-</sup> concentration for  $d = 4$  and 7 nm porous silica particles.  
 281 For  $C = 0.1$  mM, we measured a weak adsorption of surfactants on porous silica particles  $\Gamma_S = 1-3$  mg/m<sup>2</sup>,  
 282 which is equivalent to the surface excess of CTA<sup>+</sup> surfactant forming dense monolayers at the interface.  
 283 For non-spherical silica particles with  $d = 7$  nm,  $\Gamma_S$  increases up to 10 mg/m<sup>2</sup> at intermediate  
 284 concentrations and slightly decreases if  $C$  approaches the CMC ( $\approx 0.9$  mM). For spherical silica particles  
 285 with  $d = 4$  nm, the surface concentration increases up to  $\Gamma_S \approx 4$  mg/m<sup>2</sup> and significantly decreases if  $C$   
 286 approaches the CMC. It is interesting to note that at low concentrations,  $\Gamma_S$  is proportional to the pore  
 287 size, meaning that pores are filled with surfactants. In this pore size range and for surfactant  
 288 concentrations far from the CMC, the larger the pore diameter the larger the surfactant adsorption. Close  
 289 to the CMC however surfactants start to self-assemble in the form of micelles in the volume. As a  
 290 consequence, a competition between the self-assembly of surfactants in the volume and the adsorption  
 291 inside the pores of the silica particles is expected. This competition may also depend on the confinement

292 dictated by the pore size. If the pore confinement effect is very strong, micelles in the volume could  
293 hinder surfactant adsorption inside the particles' pores. For  $d = 4$  nm porous particles, the decrease of  $\Gamma_s$   
294 as a function of concentration seems in agreement with this scenario. For pore size  $d = 7$  nm, the pore  
295 confinement effect is weaker than for  $d = 4$  nm given that the micellar dimensions are about 3.5 nm, i.e.  
296 the half of the pore size, which explains the weak decrease of  $\Gamma_s$  as a function of concentration close to  
297 the CMC, see Figure 6B.

298



323 Figure 6. Adsorption amount (A) and surfactant excess concentration on the total silica Area (B) for  $d = 7$  nm (—),  
 324 and  $d = 4$  nm (!) solid particles as a function of  $\text{CTA}^+\text{OH}^-$  initial concentration.

### 325 Porous particle diffusion at the gas-liquid interface

326 At the single colloidal particle level, we have also noticed striking differences in the translational  
 327 diffusion of spherical  $d = 4$  nm porous particle at the gas-liquid interface in the absence and the presence  
 328 of  $\text{CTA}^+$  surfactants. Tracking the particle center of mass at the air-water interface, we observed  
 329 Brownian trajectories (see inset Figure 7A) and measured the mean squared displacement ( $MSD$ ), which  
 330 is plotted as a function of the lag time  $\Delta t$  in Figure 7A. Translational diffusion coefficients at the surface,  
 331  $D_s$ : can be calculated by  $MSD = 4 D_s \Delta t$ .

332 In absence of surfactants,  $D_s$  for  $d = 2$  and 4 nm pore particles agrees with the hydrodynamic prediction  
 333 for partially immersed particles at clean and flat fluid interface, see Figure 7B:<sup>40</sup>

$$334 D_s = \frac{k_B T}{k_t \eta R}, \quad (5)$$

335 where  $k_B T$  is the thermal agitation energy,  $\eta$  is the liquid viscosity and  $k_t$  is the drag factor accounting for  
 336 the particle immersion or contact angle at the interface:<sup>40</sup>

$$337 k_t = 3\pi \left[ 1 + \frac{9}{16} \cos\alpha + \mathcal{O}(\cos^2\alpha) \right] \text{ (for } 0 < \alpha < 90^\circ \text{)}. \quad (6)$$

338 For the particle diffusing in the bulk our experimental results agree with the Stokes-Brownian diffusion  
 339  $D_0 = \frac{k_B T}{6\pi\eta R} = 0.174 \mu\text{m}^2/\text{s}$ . In absence of surfactants, the good agreement between the  $1.4 < D_s/D_0 < 1.5$   
 340 experiments and the prediction shows that no additional dissipation due to contact line fluctuations (as  
 341 observed for bare silica colloids with  $1.2 < D_s/D_0 < 1.3$ )<sup>41</sup> occur on partially wetted porous particles. As  
 342 pointed out before the external porous particle surface can be regarded as a composite surface made of  
 343 hydrophilic silica and fluids. Hence, this surface presents less defects than the surface of a bare particle,  
 344 which may explain the negligible line friction due to surface defects.<sup>41</sup> As a perspective, one may wonder  
 345 if these porous particles could be good probes for passive surface microrheology since the only sources of  
 346 dissipations seem to be the viscosity.

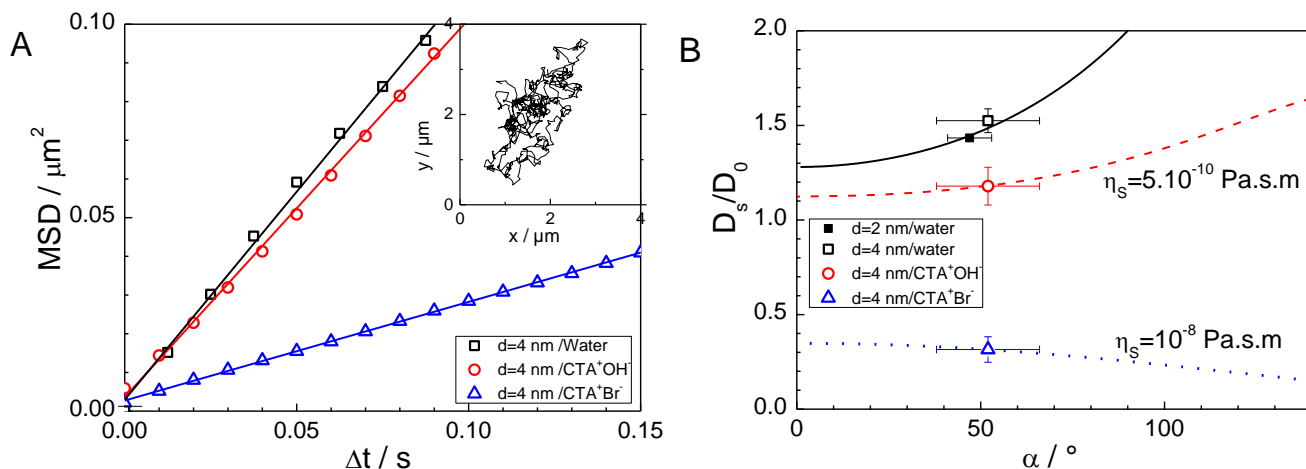
347 Surface diffusion coefficients of porous particles change significantly in the presence of  $\text{CTA}^+\text{OH}^-$  ( $C =$   
 348  $0.5$  mM):  $1.1 < D_s/D_0 < 1.2$ , and in  $\text{CTA}^+\text{Br}^-$  ( $C = 0.5$  mM) aqueous solutions:  $D_s/D_0 \approx 0.3$ , see Figure 7.  
 349 The experiments are performed at times  $\approx 3000$  s, where an increase of the gas-liquid interfacial tension  
 350 of  $5$  mN/m for  $\text{CTA}^+\text{OH}^-$ ; and no change for  $\text{CTA}^+\text{Br}^-$  were measured, see Figure 4. Hence the presence  
 351 of surfactants affect strongly the porous particle translational diffusion at the surface. For porous particles  
 352 in the presence of  $\text{CTA}^+\text{OH}^-$ , adsorption of surfactants inside the pores occurs during the porous particle  
 353 Brownian motion, whilst in the presence of  $\text{CTA}^+\text{Br}^-$  no adsorption dynamics occurs. In order to quantify  
 354 the decrease of the surface translational diffusion  $D_s$ , we use a model describing the drag felt by a  
 355 spherical particle straddling a viscous and incompressible interface possessing a surface viscosity  $\eta_s$  at  
 356 low Boussinesq numbers  $B_0 = \frac{\eta_s}{\eta R} < 1$ . The drag factor in equation 5 in this case reads:<sup>42</sup>

$$357 k_t = k_t^{(0)} + B_0 k_t^{(1)} + \mathcal{O}(B_0^2), \quad (7)$$

$$358 k_t^{(0)} \approx 6\pi \sqrt{\tanh[32(1 + \cos\alpha)/(9\pi^2)]}$$

$$359 k_t^{(1)} \approx -4\ln \left[ \frac{2}{\pi} \arctan \left( \frac{(1 + \cos\alpha)}{3} \right) \right]$$

360 For  $\text{CTA}^+\text{Br}^-$  ( $C = 0.5 \text{ mM}$ ) aqueous solutions, a surface viscosity  $\eta_s \approx 10^{-8} \text{ Pa.s.m}$  fits well the  
 361 experimental result. In the literature, a large range of values of  $\eta_s$ , from  $10^{-8}$  to  $10^{-6} \text{ Pa.s.m}$ , are reported  
 362 for soluble monolayers by surface microrheology.<sup>43</sup> Usually a large difference is also measured between  
 363 surface macro- and micro-rheology ( $\eta_s = 10^{-10} \dots 10^{-9} \text{ Pa.s.m}$ ),<sup>44</sup> which could be due to additional  
 364 dissipations or some boundary conditions not included in the analysis of the results.<sup>45,46</sup> Recent  
 365 experiments using noncontact microrheology, with completely wetted particles as probes, report  $\eta_s$   
 366  $\approx 10^{-8} \dots 10^{-7} \text{ Pa.s.m}$ ,<sup>45</sup> which agree with our results for  $\text{CTA}^+\text{Br}^-$ . For  $\text{CTA}^+\text{OH}^-$  instead our results  $\eta_s \approx$   
 367  $5 \cdot 10^{-10} \text{ Pa.s.m}$  are comparable to passive surface microrheology using partially wetted particles as probe  
 368 particles.<sup>44</sup> Given that the liquid-gas interfacial tensions are similar for  $\text{CTA}^+\text{Br}^-$  and  $\text{CTA}^+\text{OH}^-$ , one  
 369 possible explanation of the difference in  $D_s$  between the two surfactant solutions is related to the  
 370 surfactant dynamics occurring at the porous particle surface. As already pointed out before, the adsorption  
 371 of  $\text{CTA}^+\text{OH}^-$  surfactants inside the pores could lead to a local depletion of the surfactant concentration  
 372 close to the external surface of the porous particle and therefore in a smaller surface viscosity felt by the



373 particle.

374  
 375 Figure 7. (A) Mean squared displacement as a function of the lag time for  $d = 4 \text{ nm}$  porous particles at the gas-liquid  
 376 interface in pure water ( $\blacktriangledown$ ), in  $C = 0.5 \text{ mM}$   $\text{CTA}^+\text{OH}^-$  aqueous solution ( $-$ ) and in  $C = 0.5 \text{ mM}$   $\text{CTA}^+\text{Br}^-$  aqueous  
 377 solution ( $\blacktriangle$ ). The inset shows a typical particle Brownian trajectory at the surface. (B) Ratio between the surface and  
 378 the bulk diffusion coefficients as a function of the particle contact angle for the same systems shown in (A) and for  $d$   
 379  $= 2 \text{ nm}$  porous particles at the gas-liquid interface in pure water ( $\blacksquare$ ). Solid line is the hydrodynamic prediction for a  
 380 bare and clean interface. Dashed and pointed lines are drawn from a model valid for viscous and incompressible  
 381 interfacial layers with a given surface viscosity  $\eta_s$ .

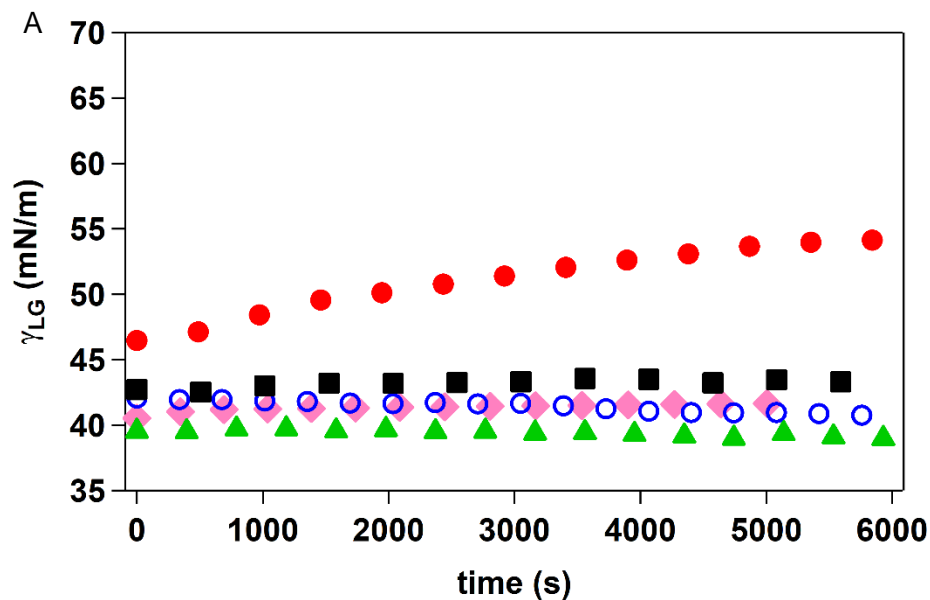
382  
 383 **Influence of the counterion on surfactant adsorption**

384 We start this section by analysing the remarkable difference in surfactant adsorption on porous particles  
 385 observed between  $\text{CTA}^+\text{OH}^-$  and  $\text{CTA}^+\text{Br}^-$ . For planar non-porous interfaces, both interfacial tensions at  
 386 the liquid-solid and liquid-gas point to a very similar behaviour for  $\text{CTA}^+$  surfactants, independently from  
 387 the counterions. However,  $\text{CTA}^+\text{Br}^-$  surfactants do not adsorb on  $d = 4$  and  $7 \text{ nm}$  porous particles, while

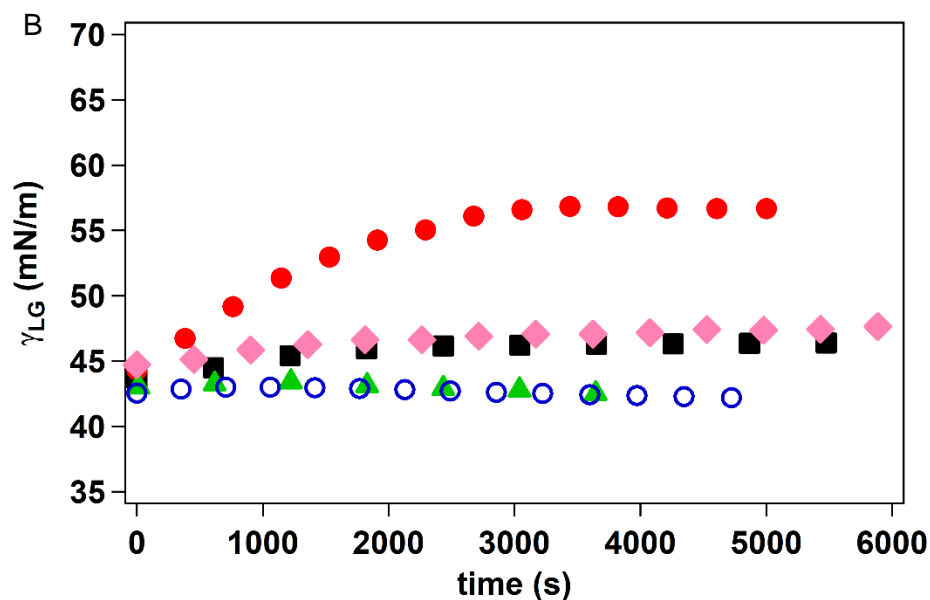
388 CTA<sup>+</sup>OH<sup>-</sup> surfactants adsorb with very high surface excess concentrations  $\approx 4\text{-}10\text{ mg/m}^2$  for  $C$  around 0.5  
389 mM.

390 To explain this striking different behavior we started to look at the pH of the solution. Adding  
391 CTA<sup>+</sup>OH<sup>-</sup> surfactants in the solution in fact alters the pH of water, which changes from 6.4 to 10.5 for  $C$   
392 = 0.5 mM. It is also well known that for planar silica surfaces, cationic surfactant adsorption usually  
393 increases if the pH increases because of the increase negative charge of the silica surface.<sup>35</sup> In order to test  
394 this hypothesis, we have added Na<sup>+</sup>OH<sup>-</sup> to a CTA<sup>+</sup>Br<sup>-</sup> solution ( $C = 0.5\text{ mM}$ ) in the presence of porous  
395 particles. The final pH measured is very similar (pH = 10.7) to the pH of CTA<sup>+</sup>OH<sup>-</sup> surfactants where a  
396 strong adsorption was observed. However also in this case, CTA<sup>+</sup>Br<sup>-</sup> surfactants do not significantly  
397 adsorb on porous silica particles, see Figure 8. It is also important to notice that for planar interfaces,  
398 CTA<sup>+</sup>Br<sup>-</sup> adsorb on silica even if the pH remains around 6.<sup>35</sup>

399 If OH<sup>-</sup> ions are not sufficient to trigger surfactant adsorption on porous particles, we consider the opposite  
400 scenario for which the ion Br<sup>-</sup> is able to hinder CTA<sup>+</sup> adsorption on silica. Therefore, in the presence of  
401 porous particles, we measure the surface tension of CTA<sup>+</sup>OH<sup>-</sup> solution adding 1 mM of Na<sup>+</sup>Br<sup>-</sup>. In this  
402 case, we observe that the surface tension of CTA<sup>+</sup>OH<sup>-</sup> (in the presence of porous particles) remains  
403 constant instead of increasing, see Figure 8. Thus, it confirms that CTA<sup>+</sup> do not adsorb inside the pores of  
404  $d = 4$  and  $7\text{ nm}$  silica particles if Na<sup>+</sup>Br<sup>-</sup> is present in the aqueous solution.



405



406

407 Figure 8. Salt effect on the liquid-gas interfacial tension as a function of time after porous particle deposition for  $d =$   
 408  $4 \text{ nm}$  particles (A) and  $d = 7 \text{ nm}$  particles (B). The surfactant concentration is fixed,  $C = 0.5 \text{ mM}$ ,  $\text{CTA}^+\text{OH}^-$  data ( $\cdot$ )  
 409 are the same as in Figure 2. Data for  $\text{CTA}^+\text{Br}^- + \text{NaOH}$  ( $\blacksquare$ ),  $\text{CTA}^+\text{OH}^- + [\text{NaBr}] = 1 \text{ mM}$  ( $\blacklozenge$ ),  $\text{CTA}^+\text{OH}^- + [\text{NaCl}]$   
 410  $= 1 \text{ mM}$  ( $\blacktriangle$ ) and  $\text{CTA}^+\text{Br}^- + [\text{NaCl}] = 1 \text{ mM}$  ( $\circ$ ) as a function of time are also shown.

411

412 In order to verify if this effect is specific to  $\text{Na}^+\text{Br}^-$ , we have also tested another salt:  $\text{Na}^+\text{Cl}^-$ . The surface  
 413 tension of  $\text{CTA}^+\text{OH}^-$  (in the presence of porous particles) in this case increases only by 1 to 3 mN/m,  
 414 which confirms a salt hindrance effect on adsorption (see Figure 8).

415 Attempting to rationalize these finding, we consider some specific ionic phenomena related to adsorption  
 416 phenomena. Some properties of  $\text{OH}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$  and  $\text{Na}^+$  are listed in table 1. The main differences between  
 417 the three negative ions are their hydration numbers (3 for  $\text{OH}^-$ , 2 for  $\text{Cl}^-$  and just 1 for  $\text{Br}^-$ ) and their



418 Jones-Dole viscosity  $B$  coefficients connected to their ability to weaken or strengthen the interfacial water  
 419 structure close to hydrophobic molecules such as the surfactant tails.  $\text{Cl}^-$  is at the border ( $B \approx 0 \text{ M}^{-1}$ )  
 420 between chaotropic  $\text{Br}^-$  ( $B = -0.04 \text{ M}^{-1}$ ) and kosmotropic  $\text{OH}^-$  ( $B = +0.18 \text{ M}^{-1}$ ) behaviors.<sup>47</sup> Hence  $\text{OH}^-$   
 421 may favor hydrophobic interactions between  $\text{CTA}^+$  hydrophobic groups, which supports the adsorption of  
 422 surface micelles; whereas  $\text{Br}^-$  leads to a weakening of these hydrophobic interactions. We have also  
 423 measured the zeta potential  $\zeta$  on bare porous particles,<sup>48,49</sup> which shows always negative values:  $\zeta = -28.5$   
 424 mV for  $d = 4 \text{ nm}$  and  $\zeta = -7.8 \text{ mV}$  for  $d = 7 \text{ nm}$ ; as expected for hydrophilic silica.<sup>50</sup> For  $\text{CTA}^+\text{OH}^-$   
 425 surfactants,  $\zeta$  remains negative for  $C = 0.25 \text{ mM}$ :  $\zeta = -19.5 \text{ mV}$  for  $d = 4 \text{ nm}$  and  $\zeta = -7.8 \text{ mV}$  for  $d = 7$   
 426 nm particles. On the contrary, in the presence of  $\text{CTA}^+\text{Br}^-$ , positive zeta potentials were measured at the  
 427 same concentration ( $C = 0.25 \text{ mM}$ ):  $\zeta = +5.3 \text{ mV}$  for  $d = 4 \text{ nm}$  and  $\zeta = +5.9 \text{ mV}$  for  $d = 7 \text{ nm}$  particles,  
 428 which points to the accumulation of positive charges on the external surface of the porous silica colloids.  
 429 Hence,  $\text{CTA}^+$  from  $\text{CTA}^+\text{Br}^-$  (or  $\text{H}_3\text{O}^+$ ) may accumulate on the silica portion of the porous particle outer  
 430 surface. This outer silica surface is very small with respect to the total porous particle surface, which may  
 431 explain the negligible change of the interfacial tension (or pH) observed in the experiments. Both the  
 432 chaotropic effect of  $\text{Br}^-$  and the repulsion due to the positive  $\zeta$  lead to a hindrance of  $\text{CTA}^+$  adsorption  
 433 inside the pores, which could explain the weak adsorption of  $\text{CTA}^+\text{Br}^-$  surfactants on porous silica  
 434 colloids.

435 Some additional specific ion effects occur on the surface of silica, where silanol groups are known to  
 436 undergo ion exchange reaction: <sup>50,51</sup>  $\text{X}^+ + \text{SiOH} = \text{X}(\text{SiO}) + \text{H}^+$  for  $\text{pH} < 8$ , where  $\text{X}^+$  is a cation ( $\text{H}_3\text{O}^+$ ,  
 437  $\text{Na}^+$  or  $\text{CTA}^+$ ), and for  $\text{pH} > 8$ ,  $\text{SiOH} + \text{OH}^- = \text{SiO}^-$ . Hence a competition between  $\text{H}_3\text{O}^+$ ,  $\text{Na}^+$  or  $\text{CTA}^+$   
 438 cations is also expected.  $\text{Na}^+$  from  $\text{Na}^+\text{Br}^-$  and  $\text{Na}^+\text{Cl}^-$  in fact competes with  $\text{CTA}^+$  in the adsorption on  
 439 silica,<sup>52</sup> which can explain the weakening of  $\text{CTA}^+\text{OH}^-$  adsorption in the presence of a sodium salt (see  
 440 Figure 8). Note that similarly to  $\text{OH}^-$ ,  $\text{Na}^+$  possesses an elevated hydration number and a positive  $B$   
 441 coefficient corresponding to a kosmotropic behavior, see Table 1.

442

	$\text{OH}^-$	$\text{Br}^-$	$\text{Cl}^-$	$\text{Na}^+$
Bare ion radius (nm) <sup>53</sup>	0.176	0.195	0.181	0.095
Hydrated radius (nm) <sup>53</sup>	0.3	0.33	0.291	0.36
Hydration number (+/-1) <sup>53</sup>	3	1	2	4-5
$B (\text{M}^{-1})$ <sup>47</sup>	+0.18	-0.04	-0.01	+0.06

443 Table 1

444

445

## 446 CONCLUSIONS

447 We have herein reported some fundamental aspects of the wetting and surface diffusion of porous  
 448 particles at the liquid-gas interface and explored the mechanisms underlying cationic surfactant  
 449 adsorption inside the particle's pores. Contact angle of porous particles at the gas-liquid interface can be  
 450 described in the framework of the Cassie model in partial wetting, and it depends strongly on the presence  
 451 of the liquid inside the pores of the particle. For pores completely filled by the liquid, the particle contact  
 452 angle is expected to be very low and porous particles may detach from the interface and diffuse in the  
 453 bulk. Particle translational diffusion at the pure water interface agrees with the hydrodynamics prediction,

454 which makes these particles ideal probes for interfacial microrheology. Porous silica colloids are already  
455 able to adsorb efficiently CTA<sup>+</sup>OH<sup>-</sup> surfactants without any chemical surface treatments on silica. We  
456 determined a significant adsorption of CTA<sup>+</sup>OH<sup>-</sup> surfactant on  $d = 4$  and 7 nm pore size colloids. The lack  
457 of adsorption for  $d = 2$  nm porous particles agrees with the presence of surface micelles and not  
458 monolayers of surfactants inside the pores of silica. We quantified CTA<sup>+</sup>OH<sup>-</sup> surface concentration and  
459 showed that for  $C < CMC$ , the adsorption increases with the pore size. Therefore, we investigated the  
460 effect of the counterion on surfactant removal in order to understand the opposite adsorption behaviour  
461 observed between CTA<sup>+</sup>OH<sup>-</sup> and CTA<sup>+</sup>Br<sup>-</sup> on porous silica colloids. pH and surface charge effects are not  
462 able alone to explain our experimental findings, which points to the importance of  
463 kosmotropic/chaotropic counterion character. Surfactant adsorption on the porous particle affects also the  
464 particle translational diffusion at the interface, which points to different boundary conditions on the  
465 particle external surface.

466 Finally, these results can be used to implement an environmental friendly strategy to remediate the  
467 surface of water from soluble and insoluble pollutants. Yet for future investigations, we plan to  
468 functionalize porous silica particles with hydrophobic groups to target contaminants that accumulate  
469 preferentially only on the water surface. Moreover, based on our expertise on self-propelled Janus silica  
470 particles at the interface,<sup>54,55</sup> we plan to investigate the role of enhanced active diffusion on the kinetic of  
471 surfactant removal.<sup>56</sup> Attention will be paid to the effect of ionic species present in the aqueous medium  
472 on the self-propulsion particle behavior.<sup>57,58</sup>  
473

## 474 **ASSOCIATED CONTENTS**

475 Supporting information

476 Non-spherical mesoporous silica particles pore size distribution, Particle deposition protocols.

477

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485

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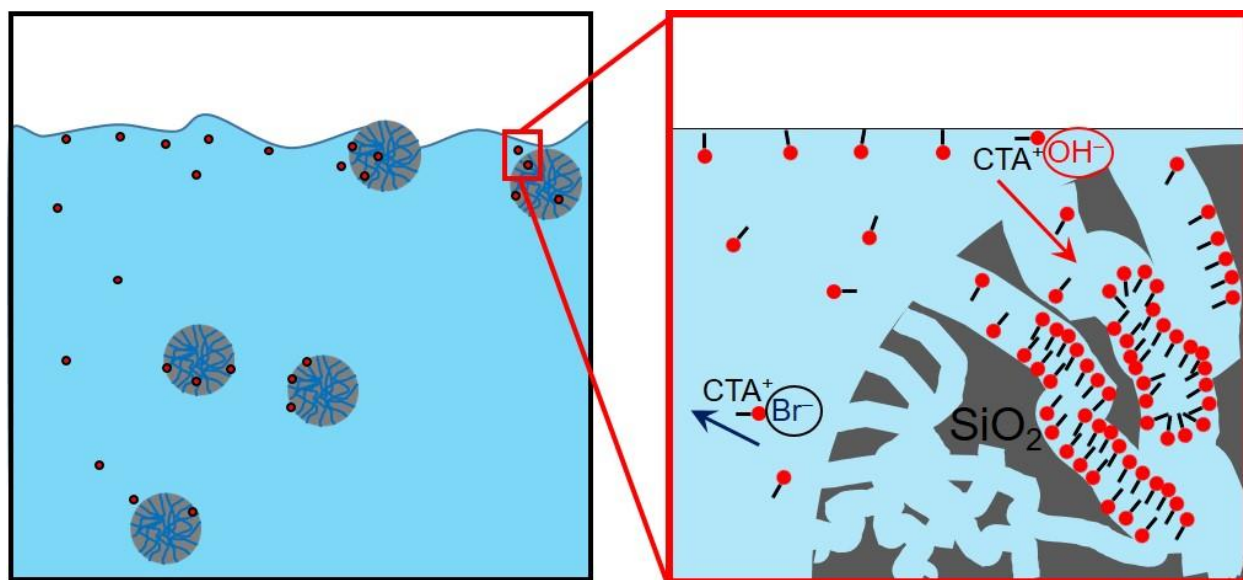
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