



Adsorption of the disinfectant benzalkonium chloride on montmorillonite. Synergistic effect in mixture of molecules with different chain lengths



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ABSTRACT

The biocide benzalkonium chloride (BAC) is a mix of cationic alkylbenzyltrimethylammonium surfactants having different alkyl chain lengths. A comparative study of adsorption on the phyllosilicate clay montmorillonite of two of these surfactants, with alkyl chains having respectively 12 C atoms (BAC-12) and 14 C atoms (BAC-14), and a mixture of both surfactants is presented in this work. Adsorption isotherms were performed for individual surfactants and for a 1:1 mixture BAC-12+BAC-14. The adsorption was investigated in an ample concentration range that covers almost seven orders of magnitude in concentrations (from 1 nM to 10 mM), range that includes environmentally relevant concentrations. Quantification of BAC was performed by HPLC–UV and LC–MS and the results were completed with powder X-Ray diffraction. The adsorption of both surfactants leads to adsorption isotherms with two well differentiated steps. The first step corresponds almost exclusively to a cation exchange process, and the binding constant is very similar for both surfactants. The second step of the isotherms is observed at higher concentrations and adsorption is mainly driven by lateral interactions between surfactant molecules. The binding constant of this step is larger for BAC-14 than for BAC-12. Adsorption from a BAC-12+BAC-14 mixture shows a synergistic behaviour, possibly due to a better packing arrangement in the interlayer. Calculations show that in natural systems silicate clays are major sorbents of BAC at low concentrations whereas binding to humic acid is predominant at high concentrations.

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1. Introduction

Benzalkonium chloride (BAC), also called alkylbenzyltrimethylammonium chloride, is a group of well-known quaternary ammonium compounds (QAC). BAC is composed by a positively charged nitrogen atom linked to a long alkyl chain (commonly from 12 to 18 carbon atoms) on one side, and a benzyl group on the other. The two last positions are occupied by methyl groups (Van de Voorde et al., 2012). A schematic representation of BAC molecular structure is given in Fig. 1. According to EPA (2006), BAC is categorized as highly toxic to fish ($LC_{50} = 280 \mu\text{g/L}$) and very highly toxic to aquatic invertebrates ($LC_{50} = 5.9 \mu\text{g/L}$) on an acute exposure basis. Chronic effects were seen in fish at a concentration of $32.2 \mu\text{g/L}$. BAC is also categorized as moderately toxic to birds and slightly

toxic to mammals. Regarding to human health risk, acute toxicity data shows that BAC is toxicity category II (moderately toxic; moderately irritating) by the oral and inhalation routes and toxicity category III (slightly toxic; slightly irritating) via the dermal route (EPA, 2006). They are also considered to be severely irritating to the eyes and skin (toxicity category I).

BAC is used as disinfectant in agricultural, food handling, commercial, institutional, industrial, residential and medical settings (EPA, 2006). Because of all these uses, BAC is easily dispersed in the environment and can pollute soils, surface water and groundwater. It is known that BAC occurs in the aquatic environment (Ferrer and Furlong, 2001). It can be freely dissolved in water or interacting with the solid components of soils or sediments, mainly minerals and organic matter. The extent of this interaction is a key factor that surely affects the mobility and fate of BAC in the environment. In fact, Ferrer and Furlong (2002) postulated that BAC in the environment would be predominantly associated with solids rather than with water. Concentrations of up to 6 mg L^{-1} of BAC have been measured in hospital effluents (Kümmerer et al., 1997) and the

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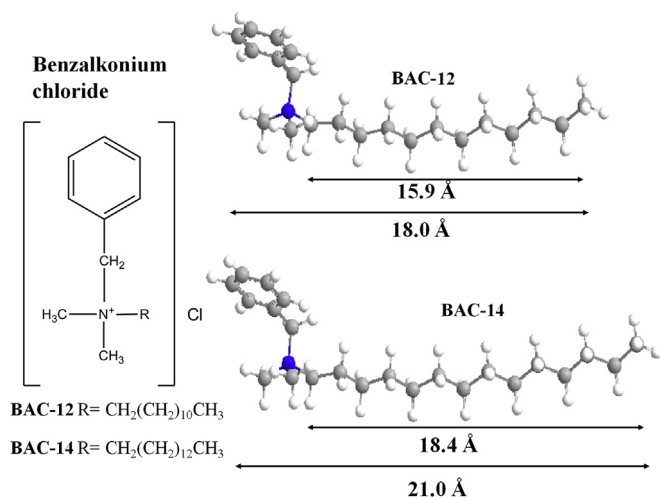


Fig. 1. Left: schematic molecular structure of BAC where R represents the long alkyl chain. Right: Molecular structure and dimensions of the two BAC molecules studied in this article, with the alkyl chain having 12 (BAC-12) and 14 (BAC-14) carbon atoms.

concentrations recorded in sediment samples range from 22 to 206 mg kg⁻¹ (Ferrer and Furlong, 2002). Several articles highlighting the environmental concern of BAC have recently appeared in the literature (Clara et al., 2007; Kümmerer, 2009; Martínez-Carballo et al., 2007; Sakar et al., 2010; Sütterlin et al., 2008; Van de Voorde et al., 2012).

Since BAC and other QAC molecules are positively charged, they show high affinity for the surface of negatively charged clay minerals such as montmorillonite. The adsorption on this solid is rather high and sometimes exceeds its cation exchange capacity, with adsorption values of around 1.6 meq g⁻¹ (Xu and Boyd, 1995; Kwolek et al., 2003). Some interaction may also occur with soil organic matter, which is also negatively charged (Matsuda et al., 2009). On the contrary, iron oxides are not expected to strongly adsorb BAC or QAC since they are usually positively charged at natural pH (Spark, 2003).

Commercial products with BAC as active agent are a mixture of homologous BAC molecules having different alkyl chains (Ferrer and Furlong, 2001). Each chain imparts to the corresponding BAC different physical, chemical and biocidal properties. Therefore, studying the adsorption of different homologues of BAC and their mixtures on clay minerals has high environmental relevance. Most of the studies that appear in the literature report the adsorption of one homologue of BAC or QAC, or compare the adsorption of different homologues with different chain length (Fejér et al., 2002; Kwolek et al., 2003; Patzkó and Dékány, 1993; Peker et al., 1995; Praus et al., 2006; Polubesova et al., 1997; Tahani et al., 1999; Xu and Boyd, 1995). However, the sorption behaviour of mixtures of BAC's has been seldom reported (Ismail et al., 2010). In addition, most of the mentioned studies were performed at relatively high concentrations of BAC, focussing the attention to the properties of synthetic organoclays, and paying much less attention to lower, environmentally relevant concentrations.

The aim of the present work is to present a comparative study of the individual adsorption on a sodium montmorillonite of a BAC with 12 carbon atoms in the alkyl chain (BAC-12), a BAC with 14 carbon atoms in the alkyl chain (BAC-14), and a mixture of BAC-12 and BAC-14. The study is performed over a wide range of aqueous concentrations, including those concentrations that could be found in the environment.

2. Materials and methods

2.1. Materials

The montmorillonite used in this study, SWy-2-Na-montmorillonite (Wyoming), was supplied by the Source Clay Minerals Repository (Columbia University, MO, USA) and was used without further purification. According to the specifications by the provider, Clay Minerals Society, the cation exchange capacity (CEC) of this clay is 0.764 meq g⁻¹. For all experiments, a stock suspension of this clay was prepared by dispersing 2.5 g of raw material in 500 mL of 0.02 M NaCl solution. The suspension was equilibrated for around 4 h and adjusted to pH 6 by addition of 0.1 M HCl. A goethite sample (910 Bayferrox) was also used in this study for comparison and was supplied by Bayer.

The surfactants used were BAC-12 and BAC-14, both of them from Fluka puriss 99.0%. As there is no literature data for the CMC (critical micelle concentration) of these surfactants in 0.02 M NaCl (used in this work), CMC was measured by dynamic light scattering with a Zetasizer ZS90 (Malvern, UK). The values for CMC were 3.8 mM for BAC-12 and 1.18 mM for BAC-14. These results are in agreement as the expected intermediate values of CMC data in 0.01 and 0.05 mol kg⁻¹ reported by Gracia et al. (2004).

All other Chemicals (NaCl, HCl, formic acid, NH₃) were analytical grade chemicals. Acetonitrile for HPLC–UV and LC–MS were HPLC grade and LC–MS grade respectively. Milli-Q water was used for HPLC–UV measurements. For LC–MS, however, glass distilled water was used because Milli-Q water was found to contain trace amounts of BAC-12 and BAC-14 detected with LC–MS as also observed by Nuñez et al. (2004).

For the studies, stock solutions at pH 6 of BAC-12, BAC-14 and a mixed BAC-12+BAC-14 solution were prepared in 0.02 M NaCl. The concentration of the BAC-12 stock solution was 12.5 mM and that of the BAC-14 stock solution was 6.3 mM. A 12.5 mM solution of BAC-14 could not be prepared because it exceeds its solubility. The concentration of the mixed stock solution was 12.5 mM for both surfactants. This was possible because the presence of BAC-12 increases the solubility of BAC-14 due to a cooperative effect (see below).

2.2. Adsorption isotherms

Adsorption isotherms were obtained by performing batch adsorption experiments. 5 mL of the montmorillonite suspension were placed in 50 mL polycarbonate centrifuge tubes. After that proper volumes of 0.02 M NaCl and appropriate aliquots of stock solutions of surfactants were added to cover concentration ranges from 0.001 mM to 7.5 mM for BAC-12, from 0.001 mM to 4.7 mM for BAC-14 and from 0.001 mM to 7.5 mM for each surfactant in the case of the mixed BAC-12+BAC-14 solution. The final volume in each tube was 20 mL. Small amounts of either NaOH or HCl solutions were added in order to reach a constant pH of 6 in all experiments. The tubes were shaken end-to-end during 17 h and the final pH was determined. Preliminary kinetic experiments showed that adsorption did not change from 30 min to 17 h, and thus data obtained after 17 h are considered as equilibrium data. In all cases, the final pH was 6.0 ± 0.1. The tubes were then centrifuged at 23425 g (14000 rpm) for 20 min and the supernatants were withdrawn and BAC-12 and BAC-14 quantified. The amount of surfactant retained by the solid (X ; mmol g⁻¹) was calculated from the equation $X = V(C_0 - C_{eq})/m$, where V (l) is the final volume in each tube, C_0 and C_{eq} (mM) are the initial and equilibrium surfactant concentrations respectively, and m (g) is the mass of adsorbent.

The concentrations of BAC-12 and BAC-14 in the supernatant were quantified by HPLC–UV in the concentration range 250–630 μM and by LC–MS in the concentration range between 1.12×10^{-3} –250 μM .

pH 6 was chosen for the experiments because this is a very common soil pH value (Zanini et al., 2009; Séquaris et al., 2013). In addition, although investigating the effects of pH on BAC adsorption is out of the scope of this article, only small changes in adsorption are expected by changing pH. This is because the positive charge of BAC molecules is independent of pH, and because structural (pH independent) charges in montmorillonite are dominant over variable (pH dependent) charges (Bradbury and Baeyens, 1997; Avena and De Pauli, 1998; Bourg et al., 2007).

2.3. HPLC–UV and LC–MS determination of BAC-12 and BAC-14

The HPLC–UV series Agilent 1100 was equipped with a Phenomenex RP18 analytical column (250 mm, 3 mm, 5 μm) at 25 °C. The mobile phase used for eluting the analytes from HPLC columns consisted of acetonitrile and 10 mM ammonium formate buffer (pH = 3.5), at a flow rate of 0.6 mL min^{-1} and detected at 262 nm. The low concentrations ranges of BAC-12 and BAC-14 were determined by LC–MS using an Agilent 1100 series with Agilent 6100 single quadrupole. The samples were separated in a Phenomenex Synergy Max-RP C12 end-capped with TMS column (10 cm, 2.00 mm, 2.5 μm , 80 Å pore size) fitted with a Phenomenex Max-RP C12 guard column (0.5 cm, 2.00 mm, 2.5 μm). The column temperature was 25 °C, and eluent flow was 0.1 mL min^{-1} . The mobile phase was acetonitrile/10 mM ammonium-formate buffer (pH 3.5) solution (70/30 v/v %) and the sample injection volume was 10 μL . The ESI parameters were +4000 V, –1 V, 8 L min^{-1} , gas temperature 200 °C and scan range 50–410 m/z with quantifier ion 304 m/z (BAC-12) and 332 m/z (BAC-14).

2.4. Powder X-ray diffraction

After adsorption isotherm experiments, the clay with adsorbed BAC was examined by powder X-ray diffraction to determine changes in the basal spacing at different loadings of BAC. Seven suspensions with C_{eq} between 6.5×10^{-5} mM to 5 mM were chosen for these measurements in order to cover a wide range of concentration and surface coverage. Diffraction traces were recorded using a Siemens D5000 diffractometer applying monochromated Co-K α radiation at 40 kV and 40 mA. For selected samples the clay pellet in the centrifuge tubes remaining after an adsorption experiment was dispersed in 1 mL of supernatant, sonicated with a probe sonicator for 1 min, and the suspension spread onto a 4 × 4 cm glass plate and allowed to dry at room temperature for 4 days before the X-ray diffraction measurement. The clay films on the glass plates were recorded from 4 to 40 °2 θ , and with a scanning speed of 0.5 °2 θ min^{-1} .

3. Results and discussion

It is well known that montmorillonite is an expandable clay that can retain chemicals such as cations, organic molecules, pollutants, etc. into the interlayer. This leads to a swelling of the clay and a change in the basal spacing (d_{001}) depending on the amount and size of the molecules retained (Spark, 2003; Giese and van Oss, 2002). Such kind of changes can be readily seen in Fig. 2(a), which shows as an example the diffraction patterns of montmorillonite with different amounts of adsorbed BAC-12. In absence of surfactant, there is a broad peak that corresponds to an average basal spacing of 12.4 Å, a value that is normal for Na⁺-exchanged montmorillonites (Kwolek et al., 2003; Tahani et al., 1999). The peak shifts to lower diffraction angles after BAC-12 is adsorbed,

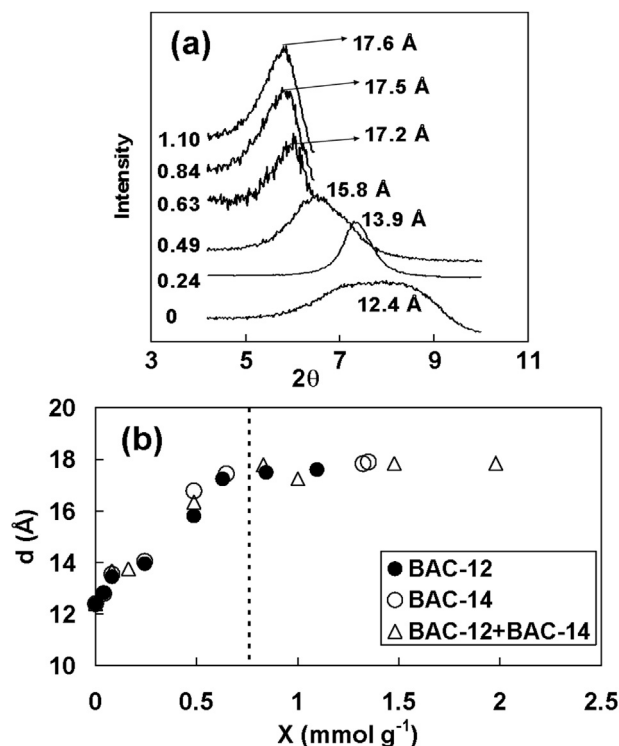


Fig. 2. (a) X-ray diffraction patterns of montmorillonite with different amounts of adsorbed BAC-12. The numbers listed to the left represent the amount of adsorbed BAC-12 in mmol g^{-1} . (b) Evolution of the d_{001} basal spacing at different surfactant adsorption on montmorillonite. The vertical dotted line indicates the adsorption values corresponding to the CEC of the clay ($0.764 \text{ mmol g}^{-1}$).

demonstrating that the adsorption of surfactant increases the d_{001} spacing as a result of BAC-12 incorporation in the interlayer.

The increase in basal spacing due to BAC adsorption shown in Fig. 2(a) was similar in the three considered cases (BAC-12, BAC-14 and BAC-12+BAC-14). Fig. 2(b) shows the evolution of d_{001} for different BAC loadings. The basal spacing changes from 12.4 Å to around 17.8 Å with loading up to 0.764 mmol g⁻¹ (vertical line in Fig. 2(b)), which is the CEC of the clay. After that, d_{001} remains constant independently of the amount of surfactant adsorbed.

Tahani et al. (1999) described a similar behaviour for the adsorption of BAC-12 on Na-montmorillonite. They observed that the basal spacing increased until the CEC of the clay was reached, with d_{001} values very similar to those presented in Fig. 2(b). In addition, they observed an extra diffraction peak corresponding to a spacing of around 34 Å for surface loadings above $1.38 \times \text{CEC}$, which was not observed in our case. Based on geometrical considerations Tahani et al. (1999) concluded that at BAC-12 loadings lower than $0.8 \times \text{CEC}$ surfactant molecules adsorb in the interlayer with a random configuration forming a monolayer of adsorbed molecules, whereas in the concentration range $0.8 \times \text{CEC}$ – $1.38 \times \text{CEC}$ adsorbed molecules form bilayers with the molecules being flat and parallel to the clay surface. They attributed the spacing of 34 Å at BAC-12 loadings above $1.38 \times \text{CEC}$ to a bilayer formed by a perpendicular arrangement of surfactant molecules. All data presented in Fig. 2 are consistent with calculations by Tahani et al. (1999) for the random and flat configurations. The absence of a peak at 34 Å rules out the possibility of a perpendicular orientation because the sum of the lengths of BAC-12 and BAC-14 molecules (Fig. 1) is much higher than the observed thickness of the interlayer space, calculated as the difference between d_{001} (around 17.8 Å) and the montmorillonite layer

thickness (around 9.6 Å). The flat orientation explains also the independence of d_{001} values with the chain length for BAC-12, BAC-14 and BAC-12+BAC-14. However, it is important to note that for chain lengths longer than 14 carbon atoms the arrangement could be different in view of the data of Xu and Boyd (1995), who found d_{001} values of around 22 Å for surfactants with chain lengths of 16 carbon atoms.

3.1. Adsorption isotherms

Fig. 3(a) shows the adsorption isotherms of BAC-12 and BAC-14. The isotherms were obtained in a wide range of concentrations: from very low concentrations as it is possible to find in the environment to rather high concentrations, above the surfactant CMC's. The adsorption increases abruptly at low C_{eq} for both surfactants. In the case of BAC-14 a well defined plateau is observed at high solution concentration, and the maximum adsorption is around 1.35 mmol g⁻¹. For BAC-12 the plateau corresponds to a maximum adsorption of around 1.10 mmol g⁻¹. In both cases these values are considerably higher than the CEC of the clay. The shape of the isotherms is typical for adsorption of this kind of surfactants on clays (Tahani et al., 1999; Patzkó and Dékány, 1993; Chen et al., 1998; Günster et al., 2006).

In order to obtain a better representation of adsorption at low solution concentrations, the same adsorption isotherms are shown in Fig. 3(b) using a logarithmic x-axis. It can be clearly observed in this figure that the adsorption of both BAC-12 and BAC-14 produces isotherms with two well differentiated steps. The first step corresponds to low surfactant concentrations and is completed at C_{eq} between 10^{-3} mM and 10^{-2} mM. The adsorption under these conditions reaches values that are very close to the CEC of the clay. The adsorption in this first step is surely due to cation exchange where sodium ions are replaced by the positively charged surfactants. The second step corresponds to relatively high surfactant concentrations and is somewhat different for the two surfactants. For BAC-14 it starts at C_{eq} around 10^{-2} mM and reaches a well defined plateau at higher concentrations. For BAC-12, the second step starts at C_{eq} between around 10^{-1} mM and 1 mM and the plateau here is not very well defined. A process different to cation exchange should take place in the second step since the loading significantly exceeds the CEC of the clay. This step is more likely due to hydrophobic interaction between adsorbed molecules.

It is useful to compare the adsorption isotherms via the parameters in isotherm equations. An overwhelming majority of surfactant adsorption studies are analysed using the Langmuir equation (Holmberg et al., 2006). The application of the Langmuir equation in their simple classical form is not possible for the system studied here because only one step would be predicted. However, it is possible to analyse the two-step isotherm by using a Langmuir equation with two terms (Gonzalez-García et al., 2005, 2004):

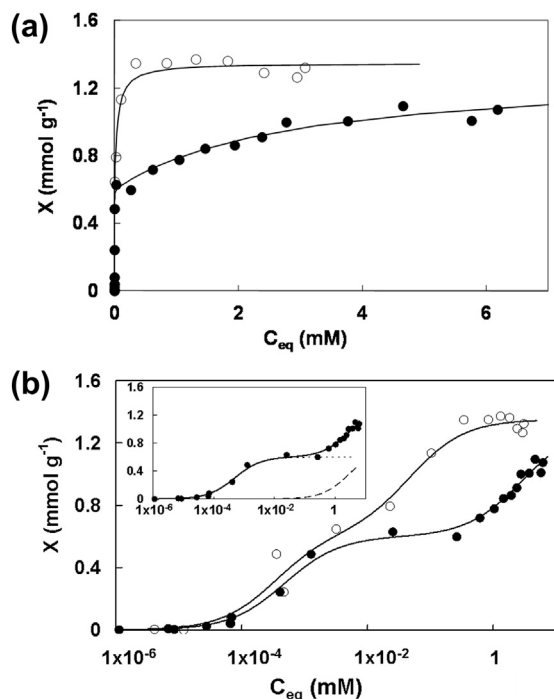


Fig. 3. Adsorption isotherms of BAC-12 (solid symbol) and BAC-14 (open symbol) to montmorillonite. Lines correspond to the fit with Eq. (1); fitting parameters are listed in Table 1. (a) Isotherm on a normal scale, and (b) Isotherm on a logarithmic scale. The insert in (b) shows the contribution of each individual Langmuir term to the adsorption of BAC-12. Solid line: total Langmuir; dotted line (Langmuir term 1); dashed line (Langmuir term 2). In supplementary material it is shown the BAC-14 isotherm with its corresponding fit with Eq. (1).

Table 1
Langmuir equation (Eq. (1)) fit to sorption isotherms of BAC-12 and BAC-14^a.

	BAC-12	BAC-14	BAC-12+BAC-14
Langmuir term 1	Log K_{L1} = 3.31 (±0.10) $X_{\text{max}1}$ = 0.60 (±0.03)	Log K_{L1} = 3.47 (±0.22) $X_{\text{max}1}$ = 0.62 (±0.12)	Log K_{L1} = 3.26 (±0.05) $X_{\text{max}1}$ = 0.65 (±0.04)
Langmuir term 2	Log K_{L2} = -0.46 (±0.15) $X_{\text{max}2}$ = 0.71 (±0.08)	Log K_{L2} = 1.32 (±0.24) $X_{\text{max}2}$ = 0.73 (±0.11)	Log K_{L2} = -0.22 (±0.04) $X_{\text{max}2}$ = 1.42 (±0.10)
r^2	0.994	0.987	0.988

^a X_{max} units are mmol g⁻¹ and K_{Li} units are mM⁻¹.

$$X = X_{\max 1} \frac{K_{L1} C_{\text{eq}}}{1 + K_{L1} C_{\text{eq}}} + X_{\max 2} \frac{K_{L2} C_{\text{eq}}}{1 + K_{L2} C_{\text{eq}}} \quad (1)$$

where X is the total amount adsorbed at the equilibrium concentration C_{eq} , $X_{\max 1}$ and $X_{\max 2}$ are the maximum adsorption capacities corresponding to each individual Langmuir term, and K_{L1} and K_{L2} are the respective Langmuir affinity constants.

The experimental results in Figures (3a) and (3b) were fitted with eq. (1) resulting in the parameters listed in Table 1. Data are well fitted by Eq. (1) resulting in r^2 values of 0.994 for BAC-12; 0.987 for BAC-14 and 0.988 for BAC-12+BAC-14. Log K_{L1} and $X_{\max 1}$ are similar for BAC-12 and BAC-14. This similarity and the close coincidence between $X_{\max 1}$ and CEC are in line with a cation exchange process in the first step. This cation exchange leads to a higher surfactant concentration close to the surface as compared to the surfactant concentration in the bulk solution, which in turn induces a kind of “micellization” process at the surface at solution concentrations far below the bulk CMC. This is what takes place in the second step where lateral (e.g. van der Waals) interactions between adsorbed molecules drive the process. Since molecular aggregation on the surface is similar to micellization one would expect the adsorption in the second step to be very dependent on the surfactant alkyl chain length. This is indeed shown by the values of log K_{L2} , which are different for BAC-12 and BAC-14, reflecting a stronger interaction between BAC-14 molecules and a weaker interaction between BAC-12 molecules. Atkins et al. (2003) in a review about the adsorption mechanism of cationic surfactants on silica showed that increasing the hydrocarbon chain length of the surfactant increases the hydrophobicity of the molecule shifting consequently the adsorption isotherm to lower solution concentrations. In agreement with this, Fig. 3 shows how the second step is starting at lower solution concentrations and is clearly steeper for BAC-14 than for BAC-12.

Fig. 4 shows the adsorption isotherm obtained with the BAC-12+BAC-14 mixture. Total adsorbed amount vs. total C_{eq} (without differentiating between BAC-12 and BAC-14) is plotted here in order to compare with data in Fig. 3(b). The fitting line was calculated with Eq. (1) and the corresponding parameters are listed in Table 1. The adsorption of the mixture also gives a two-step isotherm. The first step should also correspond to a cation exchange process since the Langmuir parameters for this step are very similar to those of BAC-12 and BAC-14. The main differences from the individual isotherms of BAC-12 and BAC-14 are in the second step. The maximum adsorption reaches values that are rather high, close to 2 mmol g⁻¹, which is reflected in the large value of $X_{\max 2}$, approximately twice the values obtained for BAC-12 and BAC-14. This high adsorption capacity of montmorillonite for surfactant molecules in the mixture indicates a synergistic interaction between BAC-12 and BAC-14. This interaction was also seen during preparation of the BAC

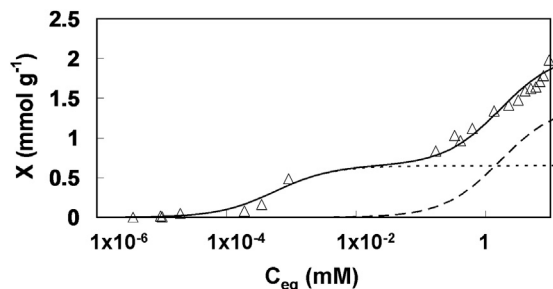


Fig. 4. Adsorption isotherm of (BAC-12+BAC-14) mixture. C_{eq} is the sum of the concentration of BAC-12 and BAC-14 in the equilibrium mixture. X is the sum to BAC-12 adsorbed and BAC-14 adsorbed in the mixture. Lines correspond to the fit with Eq. (1) and parameters listed in Table 1. The insert shows the contribution of each individual Langmuir term to the adsorption of (BAC-12+BAC-14) mixture. Solid line: total Langmuir, dotted line (Langmuir term 1), dashed line (Langmuir term 2).

stock solution, where BAC-12 increased the solubility of BAC-14. This type of synergy is well known for mixtures of homologous surfactants with different chain lengths (Schulz et al., 2006). The behaviour is explained on the basis of a better packing in the micelle core and a reduction in the hydrocarbon/water contact caused by the inclusion of a shorter homologous surfactant in the micelle of the surfactant with the longer chain (Schulz et al., 2006). This better packing seems to take place on the montmorillonite surface and in the interlayer, leading to increased adsorption without modifying the basal spacing.

3.2. Environmental implications

Many chemical and biological processes determine the retention or transport of QAC in the environment. They include adsorption, chemical degradation, and biological degradation. While all these processes are interrelated and occurring in parallel, it is clear that understanding adsorption processes is crucial to understand the mobility of these substances. The mobility of QAC depends strongly on its ability to adsorb on different components of the soil solid phase, mainly clays, metal oxides and organic matter. Not all these component have the same affinity for QAC, and thus they will contribute differently to the surfactants mobility.

As an example, Fig. 5 compares the adsorption isotherms of QAC on montmorillonite, goethite and humic acid (HA), taken as representative of clays, metal oxides and soil organic matter, respectively. For the case of montmorillonite and goethite, isotherms correspond to our BAC-12 adsorption data. For the case of HA, the isotherm corresponds to dodecyltrimethylammonium bromide (C12TAB, also called DTAB) data presented by Matsuda et al. (2009). Unfortunately there is no adsorption data in the literature for the system BAC-12/HA, and thus C12TAB (a QAC with the same chain length of 12 C atoms) is used. The line in Fig. 5 for montmorillonite was calculated with Eq. (1) and parameters in Table 1; lines for goethite and HA were calculated using a simple Langmuir adsorption isotherm with adjusted parameters $X_{\max} = 0.60 \text{ mmol g}^{-1}$ and $\text{Log}K_L = -1.0 \text{ mM}^{-1}$ for goethite and $X_{\max} = 3.43 \text{ mmol g}^{-1}$ and $\text{Log}K_L = 1.0 \text{ mM}^{-1}$ for HA. Fig. 5 shows that montmorillonite is the main responsible for the adsorption of QAC at concentrations below 0.02 M (7 mg L⁻¹) but that HA becomes the main responsible for the adsorption at concentrations higher than this value. It can be seen from that QAC will not significantly adsorb on goethite except at very high concentrations (at 5 mM, 1750 mg L⁻¹, adsorption around 0.3 mmol g⁻¹).

In order to illustrate what might happen in a natural system, a soil containing 1.5% w/w of montmorillonite, 1.5% of HA and 2% of goethite is assumed. The other components (sand, silt and the rest of the clay fraction which is not montmorillonite or other highly adsorbing clay minerals) are considered to not adsorb QAC. The percentages of QAC adsorbed on the different components of this

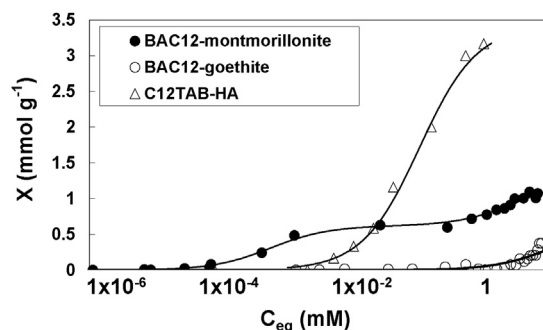


Fig. 5. Adsorption isotherm of (●) BAC-12 on montmorillonite (○) BAC-12 on goethite and (Δ) C12TAB on HA.

model soil were calculated using the corresponding parameters for the isotherms in Fig. 5 at three different equilibrium concentrations of surfactant. The data is shown in Table S1. At concentrations lower than 0.001 mM more than 92% of QAC is adsorbed on montmorillonite and the rest mainly on HA. As the surfactant concentration increases, the percentage adsorbed by organic matter becomes important, thus at 0.02 mM QAC concentration around 50% is adsorbed to montmorillonite and 50% to HA. When concentration exceeds 0.5 mM the percentage adsorbed by HA becomes higher than the adsorbed by montmorillonite. Of course increase of the montmorillonite concentration above 1.5% in the soil would make sorption to montmorillonite even more substantial. In all cases, goethite adsorbs less than 1% of surfactant. Although assuming that a soil adsorbs as a mixture of its components may be a crude approximation, these simple calculations give a first-order estimation of what may happen in a soil system, and give here a strong evidence of the significance of montmorillonite for QAC sorption.

4. Conclusions

The adsorption of BAC-12 and BAC-14 on montmorillonite starts to be significant at very low concentrations of around 10^{-4} mM and produces an adsorption isotherm with two well differentiated steps. The first adsorption step levels off at equilibrium concentrations of around 10^{-3} – 10^{-2} mM and corresponds almost exclusively to a cation exchange process. The adsorption in this step is very similar for both surfactants, either being in a mixture or not. The second step is observed at higher concentrations in the isotherms and is mainly driven by van der Waals interactions between adsorbed surfactant molecules. The interaction in this step is stronger for BAC-14 because it is the molecule with the longer hydrocarbon chain. Adsorption from a BAC-12+BAC-14 mixture shows an important synergy that may have to do with a better packing arrangement, such as it occurs with micelles in solution. The adsorption of both surfactants mainly takes place in the montmorillonite interlayer producing an increase in the basal spacing from 12.4 Å to 17.8 Å.

The use of adsorption isotherms covering a wide range of concentrations allows identifying the soil components that are more active for QAC adsorption at desired concentration. At relatively low environmental QAC concentrations, the surfactant behaviour will be controlled mainly by clays like montmorillonite; at relatively high QAC concentrations, the behaviour will be controlled mainly by soil organic matter.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jenvman.2013.04.056>.

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