



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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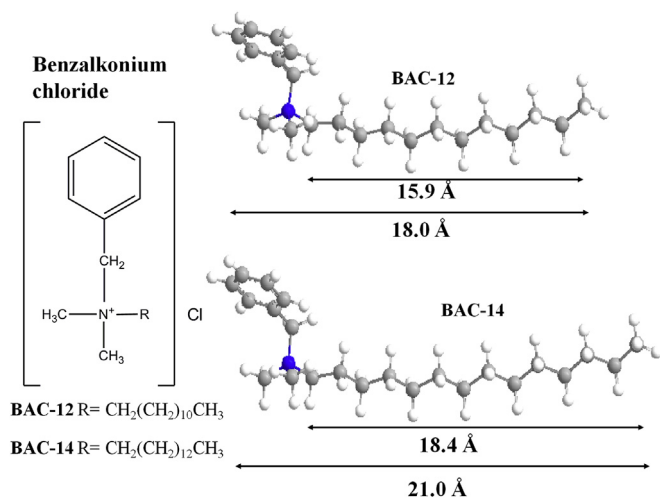


Fig. 1. Left: schematic molecular structure of BAC where R represents the long alkyl chain. Right: Molecular structure and dimensions of the two BAC molecules studied in this article, with the alkyl chain having 12 (BAC-12) and 14 (BAC-14) carbon atoms.

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.

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