Kaolinite Sorption Isotherms of Benzalkonium and Dialkyldimethylammonium Compounds under Dilute Conditions Investigated by Direct and Passive Sampling Methods

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Abstract

Cationic surfactants are widely used in various applications, making their environmental behavior a critical concern. However, soil sorption studies at environmentally relevant submicromolar concentrations remain scarce. In this study, sorption isotherms of five benzalkonium compounds (BACs) and two dialkyldimethylammonium compounds on kaolinite under dilute conditions were determined using a conventional batch-shaking and centrifugation method. In addition, the feasibility of using a polyacrylate (PA) fiber passive sampling method to measure freely dissolved surfactant concentrations in kaolinite suspensions was investigated. All kaolinite sorption isotherms were nonlinear (Freundlich exponent, 0.51–0.68), even at low surfactant concentrations (< 0.2% of the cationic exchange capacity), suggesting high sorption site heterogeneity. The kaolinite–water sorption coefficients ($K_{\mathrm{kao/w}}$) of BACs in an isosteric condition increased with alkyl chain length; however, the incremental increase in log $K_{\mathrm{kao/w}}$ per -C_2H_4- unit varied with chain length, further indicating heterogeneous sorption sites. Kaolinite sorption isotherms measured using passive sampling were comparable to those measured by direct sampling. PA fiber fouling by kaolinite particles and the high isotherm nonlinearity of PA sorption at high concentrations were identified as major sources of error.

Keywords

Cationic surfactant, clay mineral, equilibrium passive sampling, electrostatic interaction, hydrophobicity

1. Introduction

Cationic surfactants are used in a wide range of applications such as fabric softeners, cosmetics, hair care products, and disinfectants. Because removal by wastewater treatment is incomplete,[1] cationic surfactants have been widely detected in the aquatic environment.[2-4] Toxicity to aquatic organisms is relatively high; studies have shown that submicromolar concentrations (i.e., < ~100 μg/L) in water can cause toxicity to a number of aquatic organisms.[5-7] Research on their environmental fate and distribution is therefore highly needed.[7]

Sorption is a particularly important process for cationic surfactants because the surface of natural materials such as soils and sediments is often negatively charged. Past studies have indicated that cation exchange is the primary mechanism of soil sorption of cationic surfactants.[8] Natural organic matter and clay minerals are the main contributors to soil cation exchange capacity (CEC) and are thus expected to play the major role in the sorption of organic cations.[9] There are many studies in the literature on the sorption of cationic surfactants by clay minerals, reporting on various aspects such as the influence of surfactant and clay mineral types, coexisting solutes, temperature, and pH on sorption, as reviewed by Ishiguro and Koopal.[10] While previous studies investigated sorption over a wide range of surfactant concentrations,[11-18] the range was usually from μM to mM, with emphasis on a high region, around the adsorbent CEC or even up to the surfactant critical micelle concentration (CMC). This may be because clay sorption exhibits characteristic shifts passing through the CEC and CMC,[19,20] which have been a focus of research. The use of analytical techniques with low sensitivity may also be a factor limiting the concentration range. However, to understand the environmental behavior of these contaminants, knowledge of the sorption behavior at sub-μM concentrations is required, as this is the range typically found in aqueous environments and reported as the toxicity threshold.

In batch sorption experiments, particles and water are typically separated by centrifugation or filtration after sorption equilibrium has been reached. For hydrophobic (i.e., strongly sorbing) substances, incomplete separation of small, colloidal particles from water can lead to an overestimation of the truly dissolved concentration in water and thus to a significant error in the evaluation of sorption characteristics. In recent decades, equilibrium passive sampling methods using polymeric samplers such as a solid phase microextraction (SPME) fiber have been increasingly used for sorption studies.[21-23] Passive sampling methods can avoid direct sampling of water and thus avoid experimental problems associated with phase separation. However, few studies have attempted to use a passive sampling method to investigate the sorption behavior of cationic surfactants.[24,25]

The purpose of this study was twofold: to investigate the equilibrium sorption of varying structures of cationic surfactants by kaolinite at relatively low solute concentrations; and to explore the possibility of using a SPME fiber passive sampling method to measure freely dissolved concentrations in kaolinite suspensions. To this end, batch sorption experiments were performed using a conventional batch-shaking and centrifugation method to determine sorption isotherms of five benzalkonium compounds (BACs) and two dialkyldimethylammonium compounds (DADMACs) on kaolinite. Both classes of cationic surfactants are widely used as disinfectants and preservatives. Based on the experimental results, the influence of molecular structure on kaolinite sorption was discussed. In parallel to the conventional method, sorption isotherms were measured by the passive sampling method using polyacrylate (PA) fiber as a sampler. The validity of this passive method was evaluated in comparison with the conventional centrifuge method.

2. Materials and Methods

2.1. Chemicals

Benzylhexyldimethylammonium chloride (C6-BAC), benzyldimethyloctylammonium chloride (C8-BAC), and benzyldecyldimethylammonium chloride (C10-BAC) were purchased from Sigma-Aldrich (St. Louis, MO, US). Benzyldodecyldimethylammonium chloride dihydrate (C12-BAC), benzyldimethyltetradecylammonium chloride hydrate (C14-BAC), dimethyldioctylammonium bromide (C8-C8-DADMAC), and didecyldimethylammonium chloride (C10-C10-DADMAC) were from Tokyo Chemical Industry (Tokyo, Japan). The purity of these chemicals was >96%. (2,3,4,5,6-D_5)benzyldimethyldecylammonium chloride (d_5-C10-BAC), (2,3,4,5,6-D_5)benzyldimethyldodecylammonium chloride (d_5-C12-BAC), and dodecyldimethyl(D_{25})dodecylammonium bromide (d_{25}-C12-C12-DADMAC) were purchased from CDN Isotopes Inc. (Pointe-Claire, Canada). LC grade 1 M ammonium acetate and LC/MS grade water, acetonitrile, and isopropanol were obtained from Fujifilm Wako Pure Chemical Corporation (Osaka, Japan) and used for LC/MS analysis. Powder of NaCl and $CaCl_2$ as well as 1 M NaOH solution were also obtained from Fujifilm Wako Pure Chemical Corporation. Tap water was treated with reverse osmosis, further purified with an Ultrapure Water System (RFU665DA, Advantec, Tokyo, Japan), and used for conditioning of kaolinite and batch sorption experiments. All glassware was baked at 450 °C for 4 h to remove organic residues.

2.2. Kaolinite

A reference sample of kaolinite (JCSS-1101b, from Kanpaku, Utsunomiya, Japan) was obtained from the Clay Science Society of Japan. For this sample, a specific surface area of 14.82 m^2/g for this was reported, as determined by the Brunauer-Emmett-Teller method.[26] In addition, Ikegami et al.[27] measured a cation exchange capacity (CEC) of 62 meq/kg.

Exchangeable cations on kaolinite were replaced by Na^+ using NaCl, as follows. Four 50-mL polypropylene centrifuge tubes (IWAKI, AGC Techno Glass, Yoshida, Japan) each received 2 g of kaolinite and 50 mL of 1 M NaCl aqueous solution. These tubes were roller-shaken overnight at 60 rpm using a Mix Rotor VMR-5R (AS ONE, Osaka, Japan) and centrifuged at 500*g* for 5 min using an S700T centrifuge (Kubota, Tokyo, Japan). The supernatant was removed, and the remaining slurries were washed four more times with 50 mL of 1 M NaCl for 3–4 h each time. The slurries were then washed with 50 mL of water for 1 h and centrifuged at 1000*g* for 5 min. The slurries were washed two more times with water and centrifuged at 2000*g* for 30 min. The final supernatant was collected and measured for electrical conductivity using a LAQUAtwin AS-771 conductivity meter (Horiba, Kyoto, Japan), which resulted in 2.7–2.9 mS/m (~0.3 mM NaCl). The remaining slurries were frozen at −30°C and freeze-dried (FDU-1200, EYELA, Tokyo, Japan) to obtain dry powder of Na-kaolinite. For convenience, this Na-kaolinite will be referred to as kaolinite.

2.3. Polyacrylate (PA)-coated solid phase microfiber

A PA-coated glass microfiber with a coating thickness of 7 µm from Polymicro Technologies (Phoenix, AZ) was obtained by courtesy of Dr. Michiel Jonker, Utrecht University. This fiber was from the same lot as used in our previous studies.[25,28] The PA fiber was cut into 3 cm pieces, immersed in methanol containing 1% (v/v) formic acid for 1 h, rinsed with excess water, and stored in water until use. A coating volume of 2.7 µL/m was used to derive the volume-based concentration in PA.

2.4. Batch sorption experiments

An aqueous solution of 15 mM NaCl containing a predetermined amount of NaOH (~0.04 mmol per L) was aerated and used. The amount of NaOH was adjusted to give a pH of 7 when the solution was equilibrated with atmospheric CO_2. A stock of kaolinite suspension at pH 7 was prepared in the same way with 15 mM NaCl solution and a predetermined amount of NaOH (~0.15 mmol per L). The pH was checked regularly with a pH electrode (LAQUA 9615S-10D, Horiba, Kyoto, Japan) and was confirmed to be 7.0 ± 0.2. An aqueous stock solution of a single cationic surfactant was prepared by dissolving the pure substance in the 15 mM NaCl solution, which was diluted in one or two steps to 6 lower concentration stocks. No solvent carrier was used to avoid a possible influence on sorption.

For each test, 30 polypropylene (PP) microtubes (1.5 mL) were used, 14 of which received 1100 µL of kaolinite suspension, 100 µL of one of the aqueous stocks of the target cationic surfactant, and 1–2 pieces of 3 cm PA fiber. The kaolinite concentration was 4.6–18.3 mg/mL. Seven concentration levels of cationic surfactant were prepared in duplicate. In parallel, 14 PP tubes containing 15 mM NaCl solution and PA fiber, but without kaolinite, were also prepared to investigate the sorption of the cationic surfactant by the PA fiber. These no-kaolinite tubes also serve as controls to check the sorption of cationic surfactants to the tube walls. The remaining two tubes served as blanks, one with and one without kaolinite. All tubes were roller-shaken overnight, or up to 24 h, in an incubator at 25°C. Preliminary experiments with C8-BAC showed that equilibrium was reached within 3 h (Figure S1). Tubes were centrifuged for 15–30 min at 10,000 rpm (~4000*g*) using a Chibitan-II Microcentrifuge (Millipore, Darmstadt, Germany). The supernatant was pipetted into a glass vial. The fiber was collected with stainless-steel tweezers, wiped with Kim-wipe, transferred to a glass vial, and extracted with acetonitrile. For C12 and C14-BACs and both DADMACs, the sedimented kaolinite was extracted with acetonitrile containing 1% formic acid for 1 h, followed by centrifugation for 15 min. For shorter chain BACs (C6, C8, C10), kaolinite was not analyzed and the concentration sorbed to kaolinite was estimated from the mass balance calculation. The loss to the tube wall was assumed to be log-linearly related to C_w, estimated from the results of the no-kaolinite vials, and included in the mass balance calculation. The loss estimated this way was 1–13% of the C6, C8, and C10-BACs added to kaolinite suspensions and had only a small contribution to the mass balance.

For C12-BAC, the sorption experiment was also conducted with 150 mM NaCl and 5 mM $CaCl_2$ solutions. The experimental procedure was the same as described above.

2.5. Data evaluation

The data from the sorption tests were fitted with the log-transformed Freundlich model.

$$\log C_{\mathrm{kao}} = n_{\mathrm{Fr,kao}} \log C_{\mathrm{w}} + \log K_{\mathrm{Fr,kao}} \quad (1)$$

where C_{kao} (µmol/kg) and C_{w} (µM) are the concentrations of the cationic surfactant in kaolinite and water, respectively, at equilibrium. $K_{\mathrm{Fr,kao}}$ and $n_{\mathrm{Fr,kao}}$ are the Freundlich coefficient and exponent, respectively. The kaolinite/water sorption coefficient (L/kg) is defined as $K_{\mathrm{kao/w}} = C_{\mathrm{kao}}/C_{\mathrm{w}}$. Similarly, the Freundlich equation was fitted to the measured surfactant concentration in PA [C_{PA} (µM)] and C_{w}.

$$\log C_{\mathrm{PA}} = n_{\mathrm{Fr,PA}} \log C_{\mathrm{w}} + \log K_{\mathrm{Fr,PA}} \quad (2)$$

where $K_{\mathrm{Fr,PA}}$ and $n_{\mathrm{Fr,PA}}$ are the respective Freundlich parameters for PA. As shown below, the PA–water sorption isotherms slightly deviated from eq 2. Hence, for the purpose of interpolation, the following Langmuir–Freundlich equation was fitted to the data.

$$C_{\mathrm{PA}} = \frac{q_{\mathrm{max,PA}} K_{\mathrm{LF,PA}} C_{\mathrm{w}}^{n_{\mathrm{LF,PA}}}}{1 + K_{\mathrm{LF,PA}} C_{\mathrm{w}}^{n_{\mathrm{LF,PA}}}} \quad (3)$$

where $q_{\mathrm{max,PA}}$, $K_{\mathrm{LF,PA}}$ and $n_{\mathrm{LF,PA}}$ are the maximal sorbed concentration, Langmuir–Freundlich coefficient, and Langmuir–Freundlich exponent, respectively. These parameters were calibrated with the C_{PA} and C_{w} data obtained in the absence of kaolinite. Solving eq 3 for C_{w}, we obtain,

$$C_{\mathrm{w}} = \left(\frac{C_{\mathrm{PA}}}{K_{\mathrm{LF,PA}} \left(q_{\mathrm{max,PA}} - C_{\mathrm{PA}} \right)} \right)^{\frac{1}{n_{\mathrm{LF,PA}}}} \quad (4)$$

Equation 4 was used to obtain the passive-sampling-derived C_{w} from the measured C_{PA} in kaolinite suspensions. Equation 4 was only used within the calibrated range of concentrations.

2.6. Instrumental analysis

BACs and DADMACs in solutions were quantified using a liquid chromatography (LC) system (1260 Infinity II) equipped with a single quadrupole mass selective detector (MSD) (Agilent Technologies, Santa Clara, CA). All samples were spiked with an internal standard and diluted as necessary. A Kinetex EVO C18 column (2.6 µm particle size, 2.1 mm i.d. × 50 mm) was used for separation. Gradient elution was performed using aqueous ammonium acetate solution (10 mM), acetonitrile, and isopropanol as eluents. All compounds were measured with *m*/*z* values corresponding to their molecular masses. Further details of the LC and MSD conditions are provided in the Electronic Supplementary Material, S-1. The peak area of the target chemical relative to that of the internal standard (d_5-C10-BAC for C6-, C8-, and C10-BACs, d_5-C12-BAC for C12- and C14-BACs, and d_{25}-C12-C12-DADMAC for C8-C8- and C10-C10-DADMACs) was used for quantification. Calibration standards were prepared in the concentration range of 1 to 100 µg/L using acetonitrile.

3. Results and Discussion

3.1. Sorption isotherms of BACs and DADMACs on kaolinite

The measured sorption isotherms of cationic surfactants on kaolinite using the conventional method are shown in Figure 1. To our knowledge, such an extensive set of sorption isotherms on kaolinite at low surfactant loading levels (C_{kao} < 1000 µmol/kg) has not been reported in the literature. All isotherms obtained were nonlinear even at C_{kao} < 100 µmol/kg (i.e., < 0.2% of CEC), with $n_{\text{Fr,kao}} = 0.51$–0.68 (Table 1). The Freundlich equation fits the data well, and there was no clear indication of surface saturation or cooperative sorption, which is consistent with the fact that the concentrations studied (< 10 mmol/kg) were below the CEC of the kaolinite sample (i.e., 62 meq/kg).[27]

The sorption of cationic chemicals by kaolinite at low solute loading is considered cation exchange,[13,15] which is characterized by a selectivity coefficient for a given cation and follows a linear isotherm. In fact, models used to fit measured isotherms assume linearity at low surfactant concentrations.[13,19] However, closer examination of the literature data shows that linearity at low concentrations does not always hold true. For example, Xu and Boyd reported that the sorption isotherm of hexadecyltrimethylammonium by Na-kaolinite in the presence of 42 mM NaCl was linear up to the sample CEC, but nonlinear at 2 mM NaCl.[13] Kaolinite sorption isotherms of denatonium reported by Crosson et al. were linear when K^+ was the background cation, whereas they were nonlinear with Ca^{2+} and Na^+.[17] Droge and Goss[29] conducted column retention experiments with various organic cations and concluded that the sorption coefficient was generally concentration-independent, i.e., the sorption isotherm was linear ($n \sim 1$) on clay minerals including kaolinite. However, their individual data show that the sorption nonlinearity varies for individual compounds (e.g., $n_{\text{Fr}} = 0.67$–1.00 for quaternary ammoniums). Brownawell et al.[8] reported that the sorption of dodecylpyridinium on Borden Sand was extensively nonlinear ($n = 0.58$) even in the low concentration range. Overall, it cannot be generally concluded that the sorption of cationic surfactant by kaolinite is linear even at low concentrations. Therefore, it is sensible not to extrapolate sorption characteristics to concentrations outside the tested range.

A nonlinear isotherm is a manifestation of surface heterogeneity in terms of sorption sites. We speculate that the deprotonated silanol ($Si\text{-}O^-$) and the hydrophobic siloxane (Si-O-Si) are heterogeneously distributed on the silica tetrahedral facet, forming diverse sorption sites with a range of interaction properties. Recent atomic force microscopy studies have shown that the surface of the silica tetrahedral layer has a pH-dependent charge that is negative at pH > 4.[30,31] Thus, deprotonated surface functional groups are present and may contribute to the surface heterogeneity.

The isotherms shown in Figure 1 indicate that the kaolinite sorption of a longer-chain compound was always stronger than that of a shorter-chain analogue; e.g., the isotherm for C12-BAC is to the upper left of that for C10-BAC. The isotherms for C10-BAC and C8-C8-DADMAC are close to each other, as are the isotherms for C14-BAC and C10-C10-DADMAC, the respective compounds with 4 more C atoms. The sorption strength of kaolinite for cationic surfactants is further discussed in

Section 3.2 below.

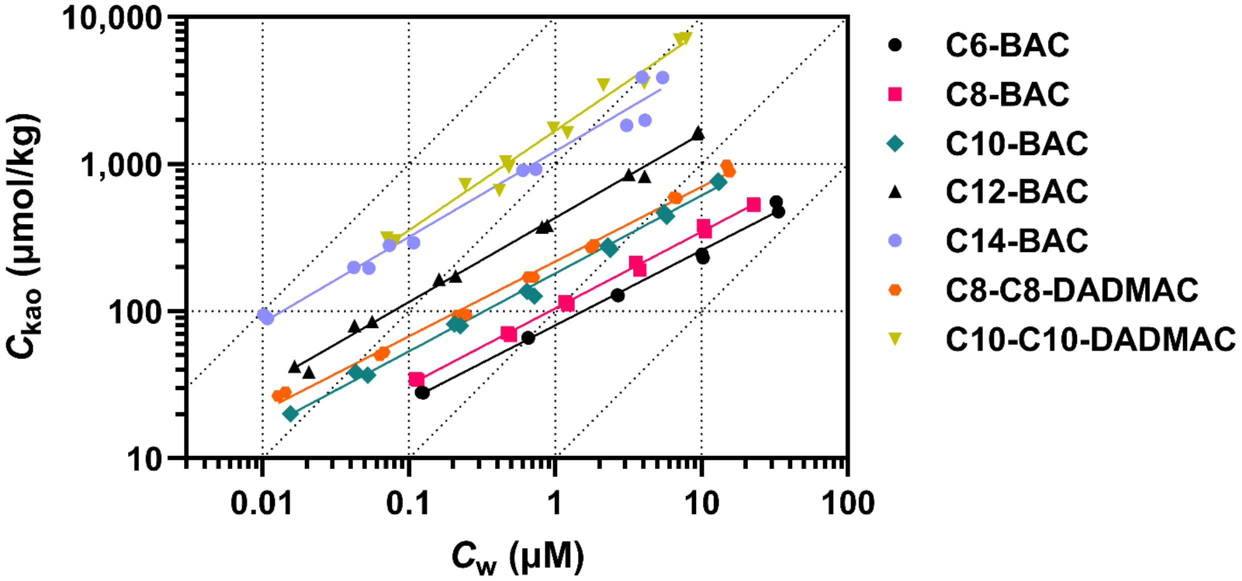

Figure 1. Kaolinite–water sorption isotherms of cationic surfactants (15 mM NaCl, pH 7, 25°C). Solid lines indicate Freundlich model fit.

Table 1. Freundlich parameters and sorption coefficients obtained for the sorption of cationic surfactants on kaolinite (15 mM NaCl, pH 7, 25°C).

	C6-BAC	C8-BAC	C10-BAC	C12-BAC	C14-BAC	C8-C8-DADMAC	C10-C10-DADMAC
Log $K_{\mathrm{Fr,kao}}$	1.90	2.02	2.26	2.64	3.09	2.34	3.23
$n_{\mathrm{Fr,kao}}$	0.51	0.52	0.53	0.57	0.58	0.51	0.68
R^2	0.989	0.995	0.991	0.987	0.938	0.989	0.960
Log $K_{\mathrm{kao/w}}$ at C_{kao} = 100 µmol/kg	1.81	2.04	2.49	3.11	3.87	2.67	3.81
Log $K_{\mathrm{kao/w}}$ at C_{w} = 0.1 µM	2.39	2.50	2.73	3.06	3.50	2.83	3.55

The type and concentration of inorganic salt dissolved in water affected the sorption isotherms of C12-BAC on kaolinite (Figure 2). An NaCl concentration of 150 mM resulted in weaker sorption by kaolinite (i.e., lower $K_{\mathrm{kao/w}}$) than 15 mM. An increase in the competing cation (Na^+) suppressed the sorption of C12-BAC, which is typical of ion exchange sorption. However, a 10-fold difference in NaCl concentration resulted in a much smaller difference in sorption strength; thus, comparing isotherms with 15 and 150 mM NaCl, $K_{\mathrm{kao/w}}$ was only 1.8 times different at C_{w} = 1 µM of C12-BAC and only 3 times different at C_{kao} = 100 µmol/kg of C12-BAC. This is inconsistent with what would be expected from the law of mass action based on the 1:1 exchange of Na^+ and C12-BAC cation.

In contrast to our results, Droge and Goss[29] reported that a 10-fold increase in NaCl concentration resulted in a 10-fold decrease in $K_{kao/w}$ for organic cations, consistent with the 1:1 exchange hypothesis. It is likely that the kaolinite sample used in the literature[29] had a different property than that used in this work. Differences in sorption properties between kaolinite samples have been reported previously for nonionic surfactants.[32] The data in Figure 2 demonstrate that 5 mM $CaCl_2$ is equivalent to 150 mM NaCl as a cation exchange competitor to C12-BAC. The stronger suppression of sorption by divalent Ca^{2+} than by monovalent Na^+ has been reported,[17] and the comparative competitive effects of 5 mM $CaCl_2$ and 150 mM NaCl are consistent with results for illite and bentonite in the literature.[29]

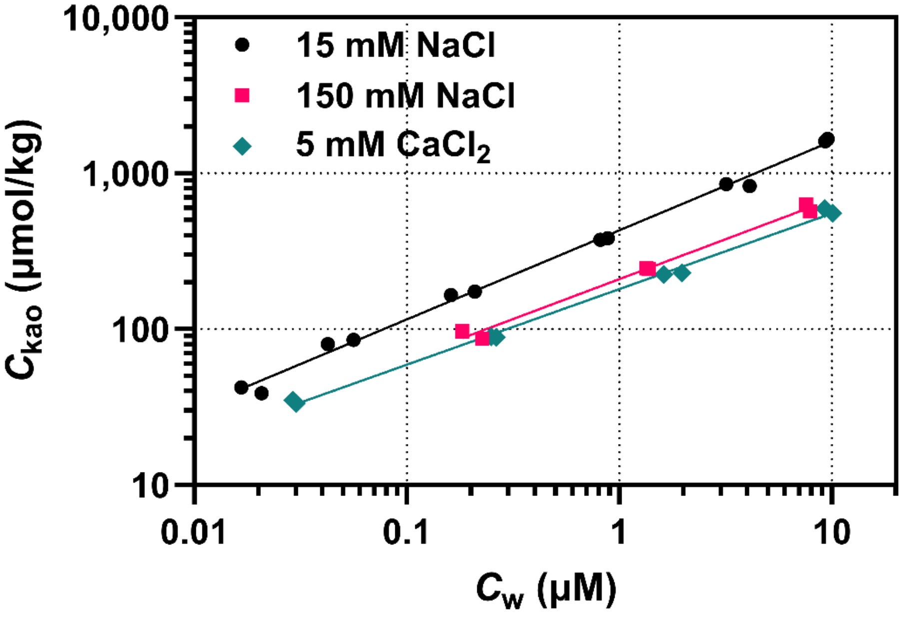

Figure 2. Salt-dependence of C12-BAC sorption on kaolinite (pH 7, 25°C).

3.2. Comparison of log $K_{kao/w}$ values

Log $K_{kao/w}$ values of cationic surfactants were calculated from the isotherm data. Since the isotherms were nonlinear, the resulting log $K_{kao/w}$ values were concentration-dependent, spanning over 1–2 log units for each cationic surfactant (Figure 3). To compare different surfactants, log $K_{kao/w}$ values in an isosteric condition (i.e., at a constant C_{kao}) were interpolated using the Freundlich equation.

The log $K_{kao/w}$ of BACs at low concentration (C_{kao} = 100 µmol/kg) increased with alkyl chain length, but the increase in log $K_{kao/w}$ per $-CH_2-$ varied with chain length. For example, log $K_{kao/w}$ increases by only 0.2 log units from C6-BAC to C8-BAC but by 0.8 log units from C12-BAC to C14-BAC. There are two possible explanations for these results. First, BACs sorb to different sorption sites of kaolinite depending on the chain length, or they sorb to the same sorption sites but in different arrangement. That is, long-chain BACs can better find sorption sites where both the positively charged head and the hydrophobic tail can interact with the kaolinite surface, whereas short-chain BACs may not be able to optimize both types of interactions simultaneously. The heterogeneous distribution of charged functional groups and hydrophobic siloxane segments, as discussed above, could explain such a misfit for short-chain BACs. Wang et al.[15] reported that the length of the shorter alkyl chain of double-chain cationic surfactants affects sorption much less than the length of the alkyl chain of a single-chain cationic surfactant, also suggesting the influence of molecular shape on kaolinite–cationic surfactant interactions. The second possibility is that organic impurities in the kaolinite sample increased the sorption of long-chain BACs. The carbon content of the kaolinite sample in this study was measured using an elemental analyzer (Flash EA1112, Thermo Fisher Scientific) and was found to be 0.03 wt%, which was below the method limit of quantification (0.1 wt%). Nevertheless, reported organic carbon/water partition coefficients (K_{oc}, L/kg) are high, particularly for long-chain BACs (>C12), e.g., 4.5–6.8 log units for different natural organic matter.[24,29] If the log K_{oc} of C12-BAC is say 6, even 0.03 wt% organic carbon could contribute significantly to the total sorption capacity of the current kaolinite sample. Thermal or chemical pretreatment of the kaolinite sample to remove organic residues prior to the sorption experiment would provide additional insight into the role of impurities in sorption, but such treatment will inevitably modify the surface of the kaolinite.

The log $K_{\mathrm{kao/w}}$ values measured in this study are compared to those reported in the literature (Figure 3). The log $K_{\mathrm{kao/w}}$ data from this study agree well with the data from Ndabambi and Kwon[33] and Wang et al.[15] This agreement is encouraging, but it may be a coincidence because these studies adopted different salt concentrations, pH values, and surfactant loading levels (see Figure 3 caption). These factors can have opposite effects on $K_{\mathrm{kao/w}}$ and cancel each other out. Note that Ndabambi and Kwon[33] also reported $K_{\mathrm{kao/w}}$ values of 4.12–7.48 for C8- to C18-BACs measured using algal toxicity responses. These values are substantially higher than any of the other measurements and are not plotted in Figure 3. The $K_{\mathrm{kao/w}}$ values from Droge and Goss[29] were measured using a column retention method with a water composition similar to that of the current study. However, their log $K_{\mathrm{kao/w}}$ values were ~1 log unit higher than our values. In the literature, a factor of ~5 difference in sorption capacity between kaolinite samples of different origin has been reported for nonionic surfactant,[32] and the result of the current study shows an even larger difference. It is interesting to note that in ref 29, benzyltrimethylammonium (C1-BAC) had a log $K_{\mathrm{kao/w}}$ value only 0.2 lower than that of C6-BAC, even though C1-BAC is five C atoms shorter than C6-BAC. This result is also consistent with the notion that the alkyl chain must be long enough to interact optimally with the kaolinite surface.

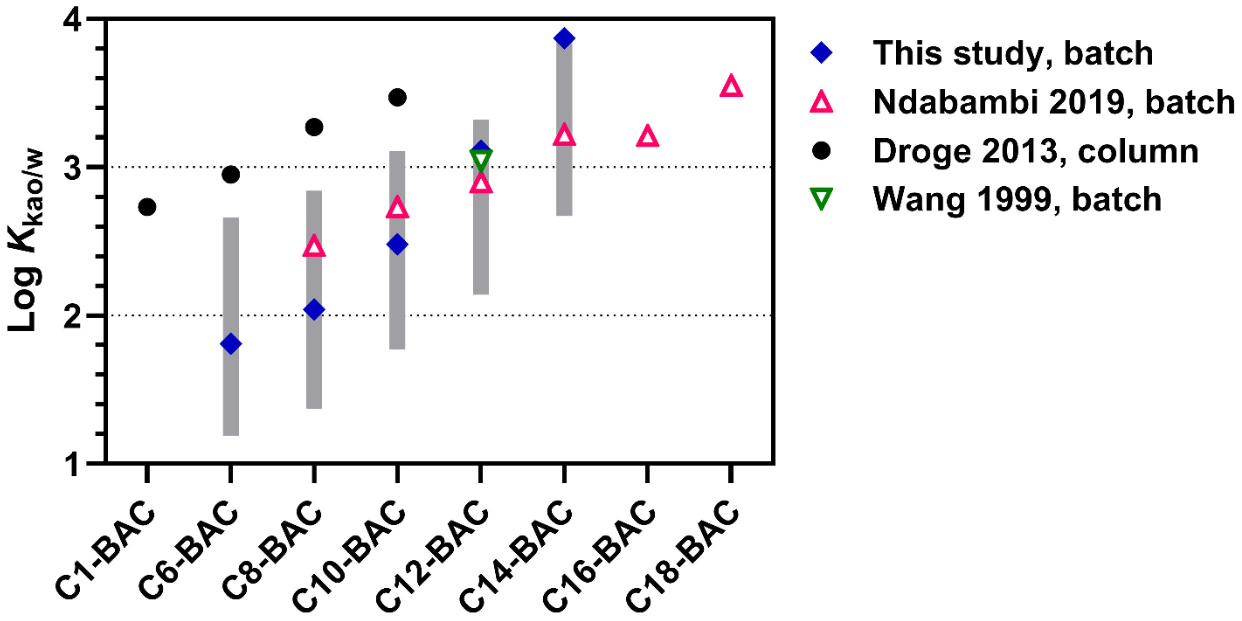

Figure 3. Range of log $K_{kao/w}$ in this study and in the literature. The bars indicate the range of log $K_{kao/w}$ in the whole concentration range investigated in this study while the blue dots indicate the log $K_{kao/w}$ interpolated for C_{kao} = 100 µmol/kg (i.e., 22–33 µg/kg, 0.2% CEC). The data source and measurement conditions are as follows. This study: pH 7, 15 mM NaCl, 25°C, CEC 62 meq/kg, loading 0.03–3% CEC; Droge 2013[29]: pH 6.1, 15 mM NaCl, CEC 40 meq/kg, loading <10% CEC (linear isotherm); Ndabambi 2019[33]: pH 8.1, 0.60 mM Na, 0.27 mM NH_4, 0.12 mM Ca, 0.12 mM Mg (OECD medium), 25°C, CEC 90 meq/kg, loading 2–16% CEC; Wang 1999[15]: pH 6, 1 mM NaCl, 20°C, CEC 20 meq/kg, loading 18% CEC.

3.3. PA–water partitioning of BACs and DADMACs

Before discussing the results of the passive sampling method, we explore the sorption characteristics of the PA fiber for cationic surfactants. The PA–water sorption isotherm for C6-BAC was nearly linear, whereas the isotherms for the other BACs became increasingly nonlinear with increasing alkyl chain length (Figure 4). The influence of alkyl chain length on sorption was generally greater for PA than for kaolinite. The isotherms were curved in the log-log plot and thus slightly deviated from the Freundlich equation (see all fitted parameters in Tables S1, S2). The isotherm nonlinearity was particularly high ($n_{Fr,PA}$ < 0.5) above C_{PA} = 1,000 µM for any compound. The higher nonlinearity observed for long-chain compounds may be due, at least in part, to the higher C_{PA} levels investigated in this study. The observed nonlinearity of PA sorption was similar to that reported for C12-BAC in the previous study.[25] As with the kaolinite shown above, the PA–water isotherms for C10-BAC and C8-C8-DADMAC overlapped, as did the isotherms for C14-BAC and C10-C10-DADMAC. These two pairs of cationic surfactants appear to have similar sorption properties.

Salt type and concentration affect the PA sorption of C12-BAC in a manner similar to kaolinite sorption (Figure S2). That is, K_{PAw} at 150 mM NaCl was lower than that at 15 mM NaCl by a factor of

2–3, depending on how the nonlinear isotherms were compared. Isotherms of 150 mM NaCl and 5 mM $CaCl_2$ were similar within a factor of 2.

The presence of kaolinite in water had negligible or only small effects on the PA–water sorption isotherms, as shown in Figure 4, where the data points in the presence of kaolinite (open symbols) are mostly within the 95% prediction interval of the Langmuir–Freundlich model fitted to the data in the absence of kaolinite. Exceptions are C6 and C8-BACs. For these short-chain BACs, the presence of kaolinite increased the sorption of BACs by PA by up to a factor of 2. Since the passive sampling method assumes no influence of suspended material on the PA sorption parameters, this variation of PA sorption will cause an error in C_w. The increase in PA sorption for C6 and C8-BACs can be explained by the kaolinite particles adhering to the PA surface, which were co-extracted and increased the apparent (measured) C_{PA}. This increase in C_{PA} is only significant for C6- and C8-BACs because PA sorption is weak relative to kaolinite sorption for these short-chain BACs. Figure 5 directly compares C_{kao} and C_{PA} in the kaolinite suspension at equilibrium and shows that PA sorption is generally stronger than kaolinite sorption, but that the difference is small or absent for C6- and C8-BACs. Kaolinite fouling on the PA surface has a negligible effect on C_{PA} for the other cationic surfactants because the adherent kaolinite particles hold only a small amount of these surfactants compared to the PA fiber.

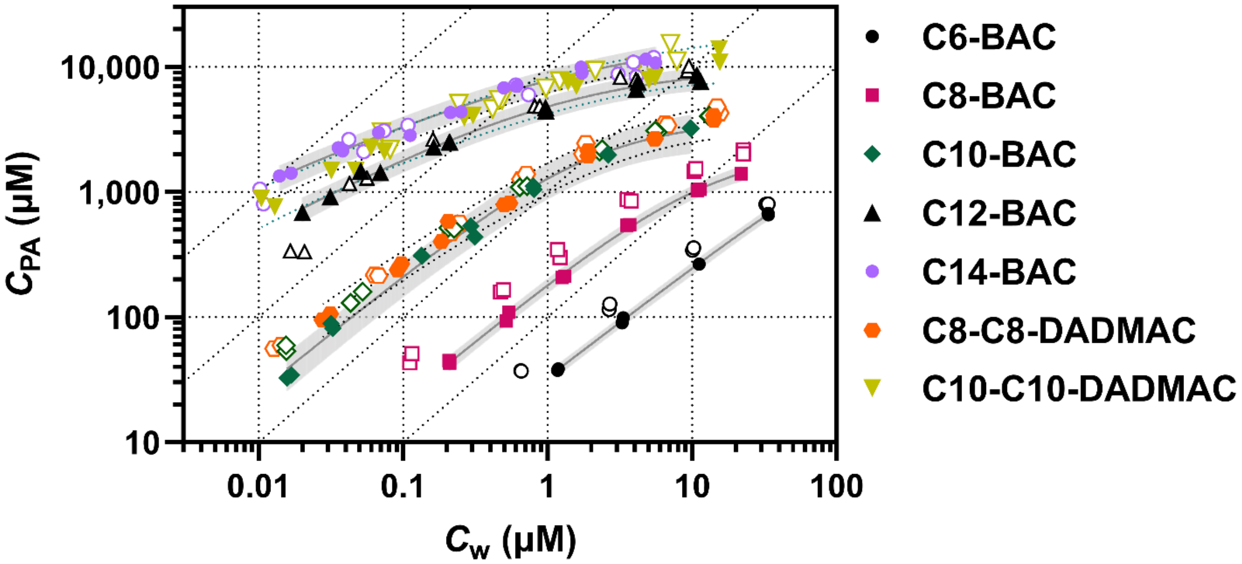

Figure 4. PA fiber–water sorption isotherms of cationic surfactants (15 mM NaCl, pH 7, 25°C). Open and filled symbols indicate the data measured in the presence and absence of kaolinite, respectively. Solid lines indicate the fit of the Langmuir–Freundlich equation (eq 4), and bands indicate the 95% prediction intervals. These lines and bands are shown only for BACs in the absence of kaolinite to avoid a crowded plot. One outlier was removed from the C6-BAC data (not shown).

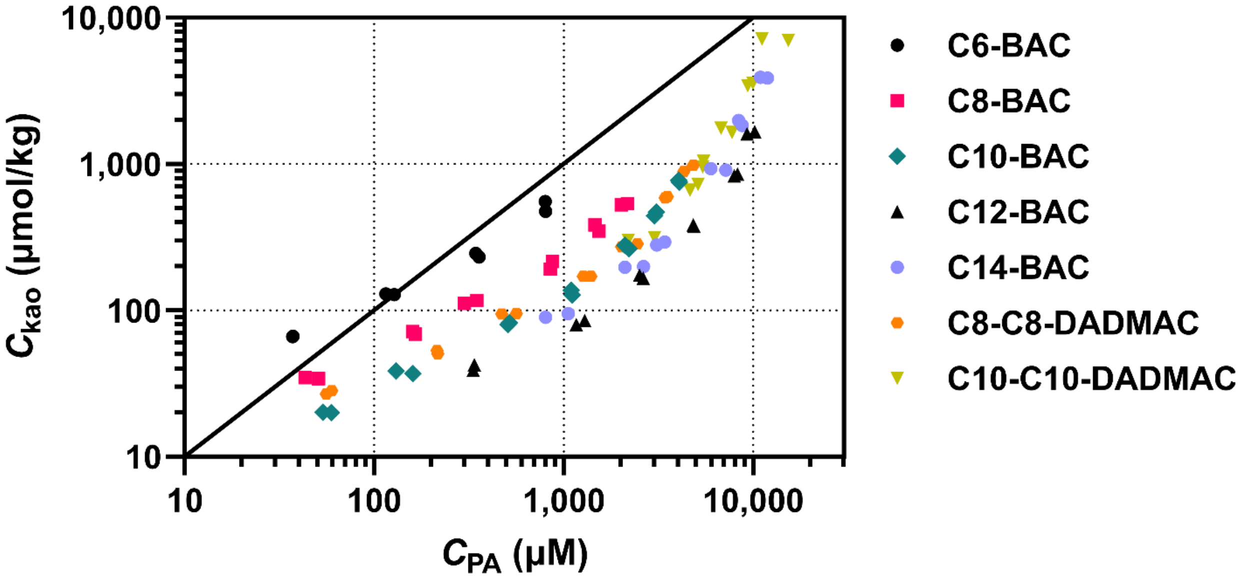

Figure 5. Kaolinite–PA fiber isotherms of cationic surfactants (15 mM NaCl, pH 7, 25°C).

3.4. Passive sampling for determination of sorption isotherms

The kaolinite–water sorption isotherms of BACs and DADMACs measured by the PA passive sampling method are compared to the directly measured isotherms (Figure 6). Overall, the isotherms measured by the two methods are in agreement. The data measured by the passive sampling method mostly fall within the 95% prediction intervals of the isotherm derived from the direct method (Figure S3). The passive sampling method overestimated C6 and C8-BAC (i.e., underestimated sorption by kaolinite), which is related to the influence of kaolinite on PA sorption as discussed above. For the other substances, passive sampling also tended to give similar or slightly higher C_w than direct sampling. Since any suspended kaolinite particles remaining in water after centrifugation would increase the directly measured C_w, the current results suggest that centrifugation effectively removed kaolinite and that direct measurement of water was not significantly affected by residual kaolinite.

There was some increased data variation for long-chain compounds such as C10-C10-DADMAC particularly at high concentrations. This result illustrates a weakness of the current approach; PA fiber sorption is increasingly nonlinear with surfactant concentration, and therefore, in the high concentration range, a small error in measured C_{PA} results in a large variation in calculated C_w. That is to say, at high concentrations, $n_{LF,PA}$ is low, and the exponent of eq 4 (i.e., $1/n_{LF,PA}$) is high, which augments the errors in C_{PA} and the sorption parameters, leading to an increased uncertainty in C_w. In addition, when C_{PA} is high and close to $q_{max,PA}$, the denominator of eq 4 approaches 0, and the estimation of C_w from C_{PA} becomes unstable.

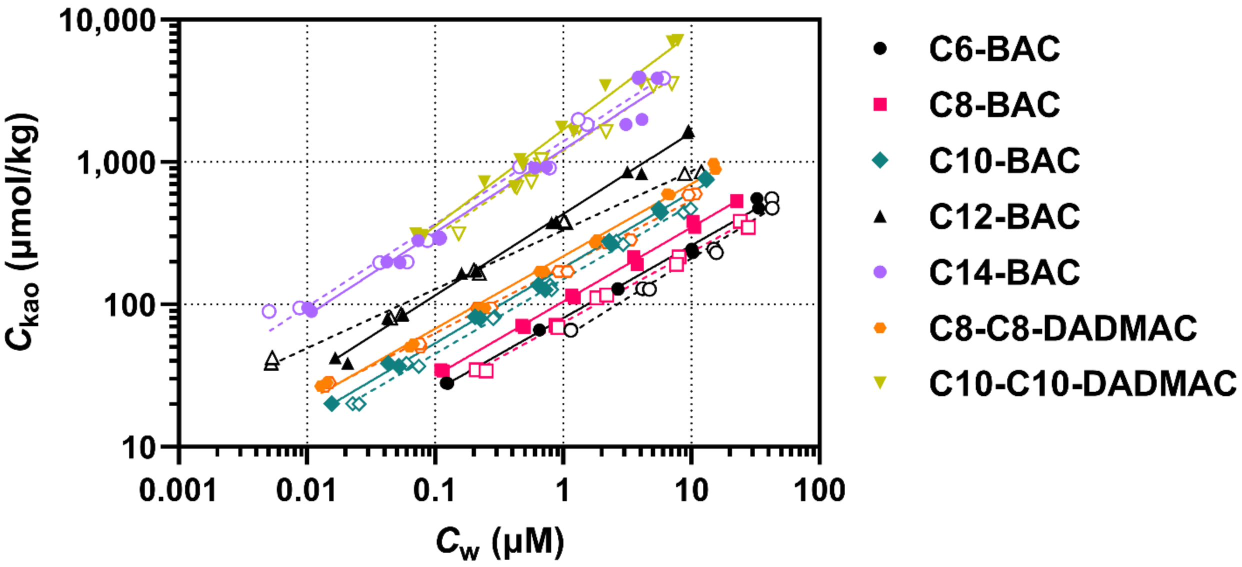

Figure 6. Comparison of kaolinite–water sorption isotherms measured by passive (open symbols) and direct (filled symbols) sampling methods. Figure S3 provides better resolution for individual compounds.

4. Conclusion

Sorption isotherms of cationic surfactants on kaolinite are nonlinear even at low solute loading conditions, indicating the heterogeneity of the sorption sites. Even in the concentration range well below CEC, sorption coefficients measured at a high concentration cannot represent those at lower concentrations. This result has implications for the transport, bioavailability, and toxicity of cationic surfactants in the environment. The nonlinear increase in sorption coefficient with alkyl chain length implies complicated mechanisms of kaolinite–cationic surfactant interactions. Further investigations with kaolinite samples of different origin or different pretreatment as well as with other (clay) minerals would shed more light on the mechanisms.

Passive sampling with PA fiber provided similar isotherms of cationic surfactants as direct sampling. Fouling with kaolinite particles and high isotherm nonlinearity at high concentrations may cause increased errors in PA fiber measurements. For kaolinite under the studied conditions, conventional centrifugation appeared to be effective in removing particles from suspension and may be more convenient than passive sampling for the compounds studied. Despite the limitations noted, passive sampling was useful in verifying the results of the conventional method in this study and could serve as an alternative method in other cases.

Data availability

All data are available in the article or in the electronic supplementary material.

Conflicts of interest

The authors declare no conflicts of interest.

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