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Structure of surfactant–clay complexes and their sorptive characteristics toward HOCs

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ABSTRACT

The influence of structural characteristics of series of surfactant–clay complexes on their sorption capacities toward naphthalene were examined, which presented some novel information about how to improve the sorption capacities of the complexes. It was shown that sorption of naphthalene on these complexes strongly depended on the conformations of the adsorbed surfactants, and the organic carbon normalized sorption coefficient (K_{oc}) value varied in a wide range (5000–20,000 L/kg) with surfactant conformation. That was, K_{oc} value first increased gradually until the maximum and then decreased sharply as the surfactant conformation developed progressively from liquidlike to solidlike (i.e., increasing surfactant packing density and ordering). At low packing density stage the surfactant aggregates have high surface/volume ratio and the attractive forces between surfactant and solute are relatively weak; whereas at high packing density stage interactions between surfactant alkyl chains are strong and more free energy is needed for creating cavities in the surfactant mediums. In both cases the sorption capacities of the complexes are weak. Thereby, the surfactant aggregates can be considered as different partition phases as their conformations changed, which then lead to the variation of K_{oc} value. Controlling the surfactant aggregates within intermediate packing density range can optimize the sorption capacities of the complexes.

1. Introduction

Sorption of hydrophobic organic compounds (HOCs) onto the surfactant modified clays (i.e., surfactant–clay complexes) has been extensively studied in the past decades due to their wide applications in environmental remediation. The surfactant–clay complexes have been considered as potential sorbents in wastewater treatment [1–4], appropriate landfill liner [5,6] and effective organic barrier for preventing down-gradient pollution of groundwater from HOCs [7,8]. All of these applications are based on the high affinity of the complexes toward HOCs, and promoting their sorption capacity is critical for improving their application efficiency.

It is known that the sorption capacity of the complexes obtained from small surfactants is mainly controlled by the exposed siloxane surface [9,10]. Thereby, any methods that can increase the surface areas of the complexes, such as selecting surfactants with smaller volume and reducing clay charge densities, will improve the sorption capacities of the complexes [9,10]. Whereas for the complexes synthesized from surfactants with long alkyl chains, the situation can be much complex. Although it is widely accepted that surfactant alkyl chains will form partition phases, which can effectively uptake HOCs [7,11–14], the sorptive characteristics of the organic phases are still under large disputation. Many investigations showed that the interlayer confined phases have quite unique sorptive characteristics comparing with the bulk liquid phases (e.g., octanol). For a given solute, it is known that the partition coefficient of a bulk organic phase is a constant, whereas the organic carbon content (f_{oc}) normalized sorption coefficient K_{oc} of the confined phases may vary over a wide range, although they are formed by the same surfactant [13–17]. Thereby, some researchers hypothesized that the affinity of the confined phases toward HOCs can be different as their structures changed [13,16,17], whereas others argued different sorption mechanisms (adsorption or partition) will contribute to the sorption processes [15,18]. As a result, the sorptive characteristics of the complexes synthesized from long alkyl chain surfactants are not clear until now, and there are no clear guides for how to improve the sorption capacities of this type of complexes.

Large numbers of investigations have also shown that structural characteristics of the surfactant–clay complexes can change greatly with surfactant loading amounts and clay layer charges [19–22]. Clarify the correlation between the structural characteristics and sorption capacities of the complexes may contribute to

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understanding their sorptive characteristics. However, structural characteristics of the complexes were not clearly characterized in great part of those reports concerning the sorption investigations; thus the proposed correlations are quite ambiguous. For example, some authors suggested that increasing surfactant packing density will improve the sorption capacities of the complexes [13,14], whereas other investigations showed that densely packed surfactant will sharply decrease the sorption capacities of the complexes [15–17].

The objectives of this work are to clarify the correlation between the structural characteristics and sorption capacities of the surfactant–clay complexes obtained from long alkyl chain surfactants, and then present some novel information for understanding the sorptive characteristics of the complexes. With these purposes, series of surfactant–clay complexes were synthesized by adsorbing different amounts of $CTMA^+$ on montmorillonite or hydrobiotite. Structural characteristics of the complexes were characterized with BET-N_2 surface area analysis, X-ray diffraction (XRD) and Fourier transfer infrared spectroscopy (FTIR). The sorption capacities of these complexes were examined by selecting naphthalene as a probe molecule. Montmorillonite and Hydrobiotite have similar layered structure but different charge densities, which will be helpful for obtaining surfactant–clay complexes with quite different structural characteristics. Results of this work may contribute to finding out ways for improving the sorption capacities of the surfactant–clay complexes.

2. Materials and methods

2.1. Materials

Montmorillonite and hydrobiotite were obtained from Inner-Mongolia (China) and Xinjiang (China), respectively. The structural formula of montmorillonite and hydrobiotite are $Na_{0.02}K_{0.02}Ca_{0.39}[Fe_{0.45}Mg_{1.10}Al_{2.51}][Si_{7.91}Al_{0.09}]O_{20}(OH)_4{\cdot}nH_2O$ and $Na_{0.25}K_{0.45}Ca_{0.04}\ [Fe_{0.58}Mg_{5.04}Al_{0.02}Ti_{0.12}][Si_{5.84}Al_{2.16}]\ O_{20}(OH)_4{\cdot}nH_2O$, respectively. Montmorillonite has a cation exchange capacity (CEC) value of 1.08 mmol/g, and each exchangeable charge site occupies interlayer surface area (A_{Mont}) about 0.57 nm^2. Hydrobiotite has a CEC value of 0.87 mmol/g. Hydrobiotite is a vermiculite–phlogopite interstratified clay mineral and the cations in phlogopite interlayers are non-exchangeable (Supplementary Data Fig. 1); thus CEC of hydrobiotite mainly contributed from vermiculite interlayers [23]. Thereby, charge sites with exchangeable cations are more density on hydrobiotite than on montmorillonite, and each exchangeable charge site occupies interlayer surface area (A_{Hyd}) about 0.35 nm^2. Cetyltrimethylammonium bromide (CTMAB) and naphthalene were of analytical grade and obtained from Shanghai Chemical Co., China.

2.2. Preparation of surfactant–clay complexes

Surfactant–clay complexes were synthesized as follows: 5.0 g of montmorillonite or hydrobiotite were dispersed in 100 mL of distilled water, and then desired amounts of CTMAB were added to saturate various percentage of the original clay's CEC. The suspensions were stirred at 50 °C for 10 h, and then aged at 25 °C for 1 week. Subsequently, the products were washed by filtration for several times and dried at 80 °C. The complexes synthesized from montmorillonite and hydrobiotite were designated as CTMA–Mont and CTMA–Hyd, respectively. CTMA–Mont complexes with different surfactant loading amounts were denoted as *x*C-Mont (*x* mean surfactant loading amount). For example, 21C-Mont represented the CTMA–Mont sample with the surfactant loading amount equal to 0.21 mmol/g, and the same notation was used for CTMA–Hyd complexes.

Table 1
Surface areas and sorption coefficient of naphthalene on the surfactant–clay complexes

Sample	BET surface area ($m^2\,g^{-1}$)	K_d ($L\,kg^{-1}$)
Mont	56.9	–
21C-Mont	14.4	740
42C-Mont	13.3	1450
64C-Mont	12.1	2420
85C-Mont	8.91	3160
106C-Mont	3.89	4070
125C-Mont	2.39	4470
147C-Mont	2.11	4050
166C-Mont	2.10	3470
198C-Mont	1.80	2720
Hyd	35.3	–
11C-Hyd	12.8	230
22C-Hyd	5.70	340
45C-Hyd	2.58	500
71C-Hyd	1.74	670
84C-Hyd	1.83	820
93C-Hyd	1.20	1000
93C-Hyd	1.12	1020

2.3. Characterization

BET-N_2 surface areas of these complexes were measured by nitrogen adsorption at 77 K with an NOVA 2000e Surface Area & Pore Size Analyzer from Quantachrome. Prior to adsorption, the samples were degassed in a vacuum at 100 °C for 12 h. The relative pressure between 0.05 and 0.35 was applied for the calculation, and the obtained values were shown in Table 1, which showed that all complexes had very small surface areas.

The XRD patterns were recorded using a Rigaku D/max-2550PC diffractometer with Cu Kα radiation. The water saturated samples were prepared as follows: a proper amount of complexes were first shaken with water at 25 °C for 4 h in a glass tubes and then the mixtures were centrifuged under 3500 rpm to collect the wet samples. The range between 1° and 20° (2θ) was recorded with a scanning speed of 2 °/min.

FTIR spectra were recorded in the 4000–400 cm^{-1} region on a Thermo Nicolet Nexus 670 FTIR spectrophotometer using KBr pressed disk technique, and the experiments were operated at a resolution of 1.0 cm^{-1}. 64 interferograms were collected for each sample.

2.4. Sorption experiments

Sorption experiments were carried out using the equilibrium technique: 0.05 or 0.1 g of the complexes powder (depending on the sorption capacities of the complexes) was combined with 20 mL solution containing 0.5–10 mg/L naphthalene in 25 mL centrifuge tubes, and then sealed with Teflon-lined caps. The tubes were shaken at 25 °C for 4 h. After centrifugation the solute concentration in supernatant was detected with UV spectrophotometer at the wavelength of 219 nm. Control experiments (without addition of sorbents or naphthalene) demonstrated that the loss of naphthalene was less than 3% during the sorption process and the released surfactant amount was far below its CMC, 0.9 mmol/L [24]. Thereby, solubilization of the solutes by the released surfactants was negligible.