

PREPARATION AND CHARACTERIZATION OF ANION–CATION SURFACTANTS MODIFIED MONTMORILLONITE

D. Chen^{1,2}, J. X. Zhu¹, P. Yuan¹, S. J. Yang^{1,2}, T.-H. Chen³ and H. P. He^{1*}

¹Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

²Graduate University of Chinese Academy of Sciences, Beijing 100039, China

³School of Natural Resources & Environment, Hefei University of Technology, Hefei 230009, Anhui, China

A series of anion-cation surfactants modified organoclays are prepared by incorporating both cationic surfactant, hexadecyltrimethylammonium bromide (HDTMAB), and anionic surfactant, sodiumdodecyl sulfonate (SDS), to montmorillonite. The added amounts of surfactant varied from 0.2 to 4.0 CEC of the used montmorillonite, similar to those reported in literature. A combination of elemental analysis, X-ray diffraction and thermogravimetric analysis is used in the characterization of the resulting organoclays. The experimental results show that anionic surfactants can not be intercalated into the montmorillonite whereas they can be loaded onto cationic modified montmorillonite, resulting in a further increase of organic carbon content of the resulting organoclays. This study demonstrates that SDS can be intercalated into montmorillonite interlayer space through the interaction with HDTMAB rather than by ion exchange. The intercalation of SDS results in an increase of the basal spacing of the resulting organoclays when comparing with HDTMAB modified montmorillonite and higher decomposition temperature of the intercalated surfactants when comparing with them in bulk state. These new insights are of high importance in the application of organoclays in the fields of remediation of polluted water and synthesis of clay based nanocomposites.

Keywords: hexadecyltrimethylammonium bromide, montmorillonite, nano-materials organoclay, sodiumdodecyl sulfonate

Introduction

Montmorillonites are widely used in a range of fields because of high cation exchange capacity, excellent swelling capacity, large specific surface area and consequential adsorption and absorption capacities [1–4]. The clay layer is negatively charged, which is counterbalanced by some exchangeable cations such as Na⁺ and Ca²⁺ in the interlayer space. Because the hydration of inorganic cations on the exchange sites causes the clay mineral surfaces to be hydrophilic, natural clays are ineffective sorbents for organic compounds [5]. To improve the affinity of clays to organic matters, modification of clay minerals with surfactants is a strategic stage for their application in the synthesis of the clay-based nanocomposites and using the resulting materials as sorbents to remove organic pollutants from water.

Organoclays are a family of potential adsorption materials for organic pollutants, prepared by exchanging the interlayer cations of clays with surfactants. Up to now, the mostly used surfactants in the synthesis of organoclays are cationic surfactants such as quaternary ammonium, which are easy to be intercalated into clay interlayer space via cation exchange [4]. When using long-chain alkyl ammonium cations, hydrophobic portion medium within the clay interlayer space can be formed and functions analogously as a bulk

organic phase. Meanwhile intercalation of cationic surfactants not only changes the surface properties of clays from hydrophilic to hydrophobic, but also greatly increases the basal spacing of the clay interlayer. Such surface property change is of high importance for the applications of the organoclays in many fields. Previous studies have demonstrated that the hydrophobic organoclays can be used as filter materials for water purification [6, 7].

Anionic surfactants (AS) are most widely used in detergent formulations and surface cleaners, which causes large quantity of organic compounds in waste water and sludge [8–10]. When these compounds are retained in soils, they are difficult to be degraded and will impede microbial processes in soil and even are inclined to be moderately toxic to invertebrates and numerous higher plants. In the past decades, how to remove these pollutants has attracted great attentions [11, 12]. As natural clay minerals are negatively charged, exchange between anionic organic ions and the metal cations within the clay interlayer space is difficult. So previous studies have focused on cationic surfactants modified montmorillonite and batch adsorption experiments of cationic surfactants modified montmorillonite show that the amount of organic pollutant removed from water depends greatly on the amount of the loaded surfactants in montmorillonite

* Author for correspondence: hehp@gig.ac.cn

[13–15]. In addition to the researches on adsorption capacity, some studies have been conducted to investigate the effect of surfactants on the enhancement of solubility of organic compounds [16, 17]. And there is a growing interest in the role of surfactants into interlayer of montmorillonite because they have influences on the behavior of pollutants in surface of organoclays [18]. However, the result shows that the mixture of anionic and cationic surfactants can increase synergistically the aqueous solubility of organic compounds. At the same time, some experiments have proved that more organic carbon can be loaded into the interlayer space of montmorillonite when both anionic and cationic surfactants are simultaneously used as modification reagents [18]. So the loading of mixed anionic and cationic surfactants in montmorillonites will increase the adsorption and absorption capacity of the resulting materials when comparing with that of single cationic modified clays.

Our previous studies of cationic surfactant modified clays show that the sorption capacity of the organoclays to model organic pollutants strongly depends on the surfactant arrangements in the montmorillonite interlayer spaces and the distribution of the loaded surfactants within the organoclays [19–21]. However, to our best knowledge, there is no detailed report about the microstructure, property of the mixed anionic and cationic surfactant modified montmorillonites, which is of high importance for their applications in the fields of materials and environmental sciences. Hence, the main aim of the present research is to investigate the microstructure and properties of anion-cation surfactants modified montmorillonite prepared under aqueous condition are investigated and elucidate the local environment and behaviors of both surfactants in gallery of montmorillonite.

Experimental

Materials

The starting calcium montmorillonite was taken from Inner Mongolia, China. The raw clays were purified by sedimentation and the fraction of $<2\ \mu\text{m}$ was collected. Its cationic exchange capacity (CEC) is $90.84\ \text{mmol}/100\ \text{g}$. Sodium montmorillonite (Na-MMT) was prepared from calcium montmorillonite by ion exchange reaction using Na_2CO_3 . All reagents (Fig. 1) except SDS (chemical grade, from Shanghai Lingfeng chemical reagent Co., Ltd.) are of analytical grade and provided by Tianjin Damao Chemical Reagent Co., Ltd.

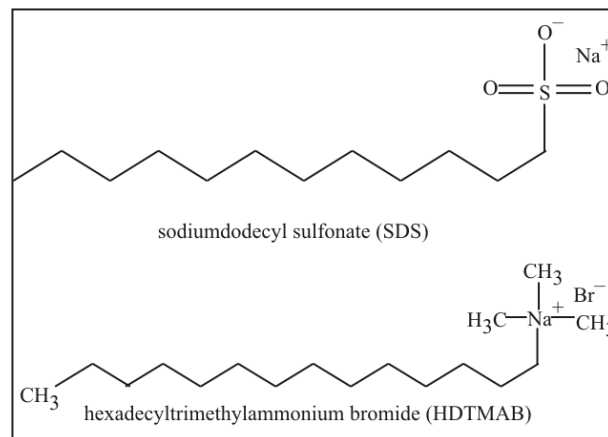


Fig. 1 Chemical structure of the used surfactants

Preparation of organoclays

The HDTMAB modified montmorillonites were prepared by the following method. A desired amount of HDTMAB was added into hot distilled water firstly and a clarified surfactant solution was obtained. Then a desired amount of Na-MMT was added into the above mentioned surfactant contained solution and the mixture was stirred slightly in order to avoid the yield of spume in an 80°C water bath for 8 h. The water/Na-MMT mass ratio is about 10. The suspension was subsequently washed with distilled water for 7–8 times. The moist solid material was dried at 80°C and ground. These HDTMAB modified organoclays were labeled as 1.0C, 2.0C, 3.0C and 4.0C. The prefix number denotes the amount of the added surfactant expressed as the montmorillonite's CEC. For example, sample 1.0C means that the organoclay was prepared in the reaction solution containing 1.0 CEC of surfactant.

The anion–cationic surfactants modified montmorillonites were prepared by the following method. The HDTMAB modified organoclays were further modified by anionic surfactant (SDS) using a similar way as above-mentioned. The resulting organoclays were labeled as 0.5C/0.5S, 1.0C/1.0S, 2.0C/1.0S and 3.0C/3.0S, etc. Similar to the labeling way for HDTMAB modified organoclays, the first and second numbers denote the amounts of the added cationic and anionic surfactants (expressed using CEC), respectively.

To compare with the organoclays prepared from only cationic surfactant, and both anionic and cationic surfactants, an organoclay was prepared under the condition of only adding 1.0 CEC of SDS and the product was denoted as 1.0S.

Methods

Elemental analysis (carbon and sulfur) was conducted on a Vario EL III element analyzer. Before measurement, all samples were preheated at 105°C for 2 h. Silicon is determined directly by means of the molybdenum blue method. XRD patterns of montmorillonite and the resulting organoclays were obtained on a Rigaku D/Max 2000 X-ray Diffractometer, using $\text{CuK}\alpha$ radiation ($\lambda=0.15418$ nm) at 40 kV and 30 mA with a scan speed of 3°min^{-1} and 2θ range of $1-20^\circ$.

Thermogravimetric analysis of the samples was performed on a Netzsch STA 409PC operating at ramp $5^\circ \text{C min}^{-1}$ from room temperature to 700°C under a high purity flowing nitrogen atmosphere with $60 \text{ cm}^3 \text{ min}^{-1}$. Approximately 20 mg of finely ground sample was heated in a capped alumina crucible. Repetitive analyses were undertaken. The thermogravimetric curve fitting was performed using the Netzsch 'Peak Separation' software (ver. 2004. 02).

Results and discussion

Elemental analysis

The elemental analysis results of the organic carbon for sodium montmorillonite and the resulting organoclays are presented in Figs 2–4. It can be found that the carbon content of sample 1.0S is 0.5%, similar to that of Na-MMT. This suggests that the anionic surfactant (SDS) can not be intercalated into montmorillonite interlayer spaces and absorb on the clay surface, as both montmorillonite and surfactant are negatively charged. This is in agreement with the evidence from XRD pattern of 1.0S, in which no interlayer expansion of montmorillonite is observed (Fig. 5a).

Our previous studies have shown that cationic surfactants are easily be intercalated into montmorillonite interlayer spaces via ion exchange. The amount of the intercalated surfactants increases with an increase of the added amount of surfactants, which causes an

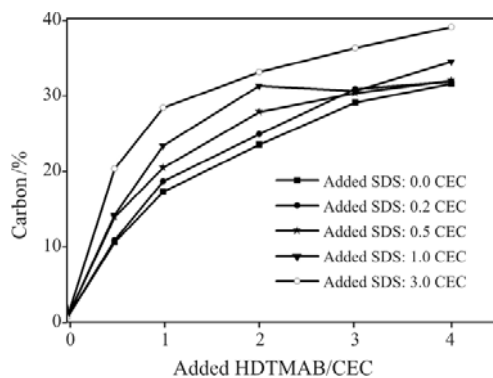


Fig. 2 The carbon content of modified organoclays

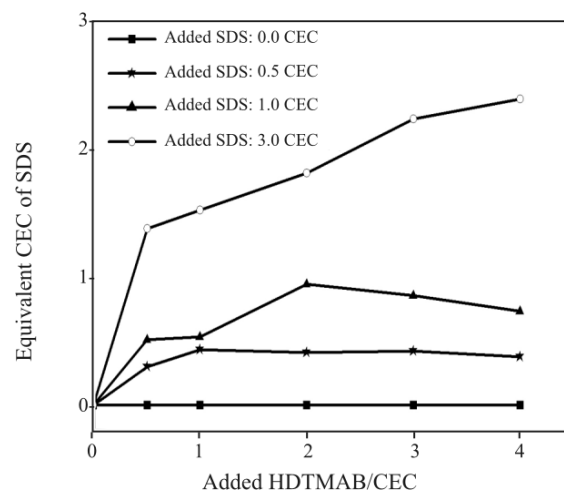


Fig. 3 The equivalent CEC of SDS in the resulting organoclays

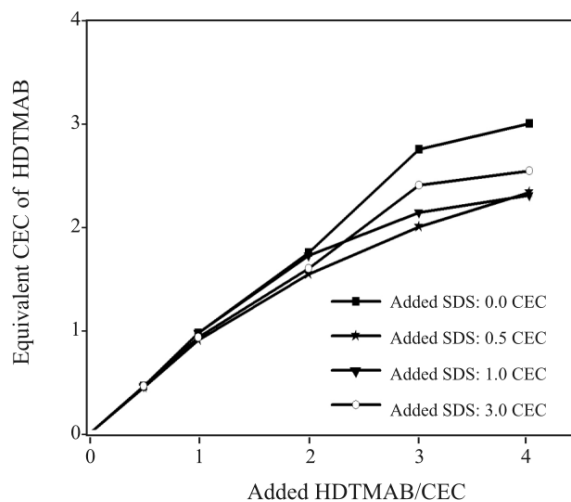


Fig. 4 The equivalent CEC of HDTMAB in the resulting organoclays

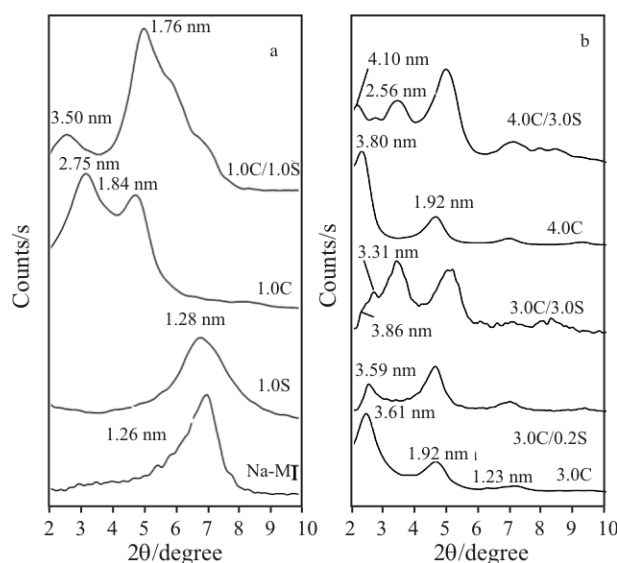


Fig. 5 XRD patterns of a – Na-MMT and b – the representative organoclays

expansion of basal spacings [19, 22]. Interestingly, when HDTMAB modified montmorillonites are used as precursors and SDS is added in the solution containing the cationic surfactant modified organoclays, the carbon contents of the resulting products increase with an increase of the added anionic surfactant amounts, compared with the corresponding organoclays modified with only HDTMAB. For example, the carbon content of 1.0C/0.2S is 18.6%, more than that of 1.0C (17.0%). When adding 1.0 times of SDS, the carbon content of 1.0C/1.0S increases to 23.3%, which is more than that of 2.0C (23.0%). These results suggest that a prominent contribution on carbon content increase of the resulting products is from the loading of SDS and there is a synergistic effect between anionic and cationic surfactants.

As shown in Fig. 2, the carbon content of 0.5C/0.5S is 13.9%, which is less than 17% of 1.0C. In contrast, the carbon content of 1.0C/0.5S is about 20.4%, obviously more than that of 0.5C/0.5S. This implies that the main contribution of carbon content increase in the resulting organoclay is from the cationic surfactant. For the series of both anionic and cationic surfactant modified organoclays, prepared using 0.5C as precursors, the carbon contents are 13.9% (0.5C/0.5S), 13.0% (0.5C/1.0S), 20.3% (0.5C/3.0S), respectively. Here, it can be found that the cationic surfactant have a principal role on the carbon content of the resulting organoclays.

Figures 3 and 4 show the amount of HDTMAB and SDS equivalent CEC of montmorillonite loaded in the resulting organoclays. Since silicon content is stable in synthesis, equivalent mass (k) is set as silicon content ratio of organoclay to Na-MMT in order to retrieve the original added amount of Na-MMT in organoclay as Eq. (1).

$$k = \frac{C_{\text{Si}}}{^*C_{\text{Si}}} \quad (1)$$

$$^eC_{\text{S}} = C_{\text{S}} - ^*C_{\text{S}}k \quad (2)$$

$$^eC_{\text{C}} = C_{\text{C}} - ^*C_{\text{C}}k \quad (3)$$

Equivalent CEC of SDS (m) and that of HDTMAB (n) is calculated using the Eqs (2) and (3).

$$m = \frac{^eC_{\text{S}}}{90.84k \cdot 10^{-3}} \quad (4)$$

$$n = \frac{\frac{^eC_{\text{C}}}{12} - \frac{^eC_{\text{S}} \cdot 12}{32}}{90.84k \cdot 10^{-3}} \quad (5)$$

where C_{Si} : total silicon percentage of the sample; C_{C} : total organic carbon percentage of the sample; C_{S} : total sulfur percentage of the sample; $^*C_{\text{Si}}$: silicon percentage of Na-MMT; $^*C_{\text{C}}$: carbon percentage of Na-MMT; $^*C_{\text{S}}$: sulfur percentage of Na-MMT; $^eC_{\text{C}}$: contribution on carbon percentage by both surfactants; $^eC_{\text{S}}$: contribution on carbon percentage by SDS; 90.84: amount of CEC (mmol/100 g).

From Figs 3 and 4, it can be seen that more and more SDS are loaded onto montmorillonite with an increase of HDTMAB concentration in the preparation solutions. For example, when the total amount of the added SDS is 3.0 CEC and the added HDTMAB increases from 1.0 to 2.0, 3.0, 4.0 CEC, the loaded SDS increases from 1.53 to 1.82, 2.24, 2.40 CEC, respectively. However when a relatively high amount of intercalated HDTMAB (more than 2.0 CEC loaded surfactants) is realized, it can be found that the amount of the intercalated HDTMAB decreases with an increase of the loaded SDS. For example, the equivalent CEC of HDTMAB decreases from 2.77 to 2.41 for 3.0C to 3.0C/3.0S and 1.73 to 1.61 for 2.0C/1.0S to 2.0C/3.0S. Here, it can be seen that, in the case of the same HDTMAB concentration in the preparation solutions, the increase of SDS concentration results in a decrease of the amount of the loaded HDTMAB whereas the amount of the loaded SDS increases. But the total carbon content in the resulting organoclays increases with the increase of SDS concentration in the preparation solutions.

X-ray diffraction analysis

Previous studies [23, 24] have demonstrated that the surfactant ions/molecules not only enter into the clay interlayer spaces but also are adsorbed on the clay external surface. To prove surfactants loaded in the galleries of the resulting organoclays, the XRD analysis is a powerful technique. When the interlayer sodium ions are exchanged by HDTMA⁺ an expansion of montmorillonite interlayer occurs, indicated by XRD patterns [19, 22]. In Fig. 5a, Na-MMT displays a basal spacing of 1.26 nm, which is almost identical to our previous report [19]. As shown in Fig. 5a, 1.0S displays a basal spacing at 1.28 nm, almost identical to that of Na-MMT, suggesting that there is no SDS intercalated into montmorillonite interlayer spaces. This proposal is supported by the elemental analysis results.

The XRD pattern of 1.0C shows a broad diffraction peak centered at 2.75 nm and a shoulder at 1.65 nm. With the increase of the loaded surfactant, especially SDS, two or more peaks appear and bigger basal spacings are observed. The broadened reflections are acknowledged to interlayer charges [25, 26]. However,

for 1.0C/1.0S, the basal spacing is about 3.50 nm while the (002) reflection with a d value of 1.76 nm appears (Fig. 5a). Compared with the XRD pattern of 1.0C, a prominent increase of the basal spacing of 1.0C/1.0S is observed and this is resulted from the intercalation of SDS.

On the other hand, as shown in Fig. 5b, the basal spacing of 3.0C is ca. 3.62 nm. For 3.0C/0.2S and 3.0C/3.0S, the basal spacings are 3.60 and 3.68 nm, respectively. It can be seen that their basal spacings are similar, resulting from the high packing density [19] and the difficulty for the intercalation of SDS. For 4.0C, it exhibits a highly ordered stacking as indicated by the regular 001 reflections at 3.80, 1.92 and 1.27 nm, corresponding to d_{001} , d_{002} and d_{003} , respectively. Similar phenomenon is also observed in the XRD pattern of sample 3.0C. These observations are similar those reported in literature [19, 22]. However, after the secondary modification with SDS, the series of regular 001 reflections disappear and a slight increase of basal spacings is observed in the XRD patterns of the corresponding organoclays (i.e., 3.0C/3.0S and 4.0C/3.0S), reflecting that SDS has been intercalated into the clay interlayer spaces and the loading of SDS has an influence on the arrangement of the pre-intercalated cationic surfactants. The XRD pattern of 4.0C/3.0S shows a maximum d_{001} value at 4.1 nm, which is the largest one compared with those reported in literature [27]. Our proposal about the intercalation of SDS into clay interlayer spaces deduced from XRD patterns is in agreement with that from elementary analysis.

Thermogravimetric analysis

Thermal analysis using thermogravimetric techniques (TG) enables the mass loss steps, the temperature of the mass loss steps and the mechanism for the mass loss to be determined [28, 29]. Thermo-analytical methods may provide a measure of the thermal stability of materials and their mass loss [30–33]. Figure 6 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of Na-MMT, HDTMAB, SDS and the representative organoclays and the mass losses corresponding to different mass

loss steps are presented in Table 1. As shown by the TG curve of neat HDTMAB, the decomposition of the neat surfactant occurs at ca. 268°C while SDS shows a large temperature contrast for decomposition. It can be seen from that HDTMAB can be decomposed completely above 350°C while SDS still has a residual about 25.0% after 700°C (Fig. 6), indicating the sodium and sulfur contents in SDS is not completely decomposed under a N₂ atmosphere.

As shown by the TG curve, Na-MMT is relatively stable in the temperature range of 200–550°C, i.e. the mass loss of the resulting organoclays in this temperature range should be attributed to the evaporation/decomposition of the loaded surfactant. The mass loss of Na-MMT from room temperature to 200°C, centered at ca. 110°C in DTG curve, corresponds to the dehydration of physically adsorbed water and water molecules around metal cations such as Na⁺ on exchangeable sites in montmorillonite [34]. From Table 1, it can also be found that the mass loss of Na-MMT in this step is much more than that of organoclays. This reflects a surface property transformation of montmorillonite from hydrophilic to hydrophobic, resulted from the modification of surfactants.

The thermogravimetric analysis of HDTMAB modified montmorillonite has been reported in literature [23]. Previous studies demonstrate that there is only one mass loss step occurring at 380–400°C, corresponding to the decomposition of the intercalated surfactant, when the amount of the loaded surfactant is relatively low (e.g., 0.5 CEC of HDTMAB) [31]. With the increase of the loaded surfactant, another mass loss step is observed, attributed to the adsorbed surfactants [23, 31]. However, in the present study, both cationic and anionic surfactants are loaded into montmorillonite and the obtained TG and DTG curves are significantly different from those of only HDTMAB modified montmorillonite as reported in literature [23].

As shown in Fig. 6, the DTG curve of 0.5C/0.5S displays two peaks centered at 108 and 398°C, corresponding to the losses of physically sorbed water and the decomposition of the intercalated surfactants, respectively. The prominent decrease of mass loss in the first step (centered at 108°C) results from the

Table 1 The mass loss in the resulting thermogravimetric curves of representative organoclays

| Samples | Mass loss/% | | | | |
|-----------|-------------|-----------|-----------|-----------|-------|
| | 30–200°C | 200–400°C | 400–500°C | 500–700°C | Total |
| Na-MMT | 9.6 | – | – | 5.2 | 14.8 |
| 0.5C/0.5S | 5.5 | 7.0 | 6.2 | 6.2 | 24.9 |
| 0.5C/3.0S | 4.8 | 7.5 | 17.5 | 3.5 | 33.3 |
| 2.0C/2.0S | 2.2 | 32.2 | 16.0 | 1.4 | 51.8 |
| 3.0C/3.0S | 2.2 | 43.6 | 15.6 | 1.1 | 62.5 |
| 4.0C/3.0S | 2.5 | 45.3 | 18.3 | 0.5 | 66.6 |

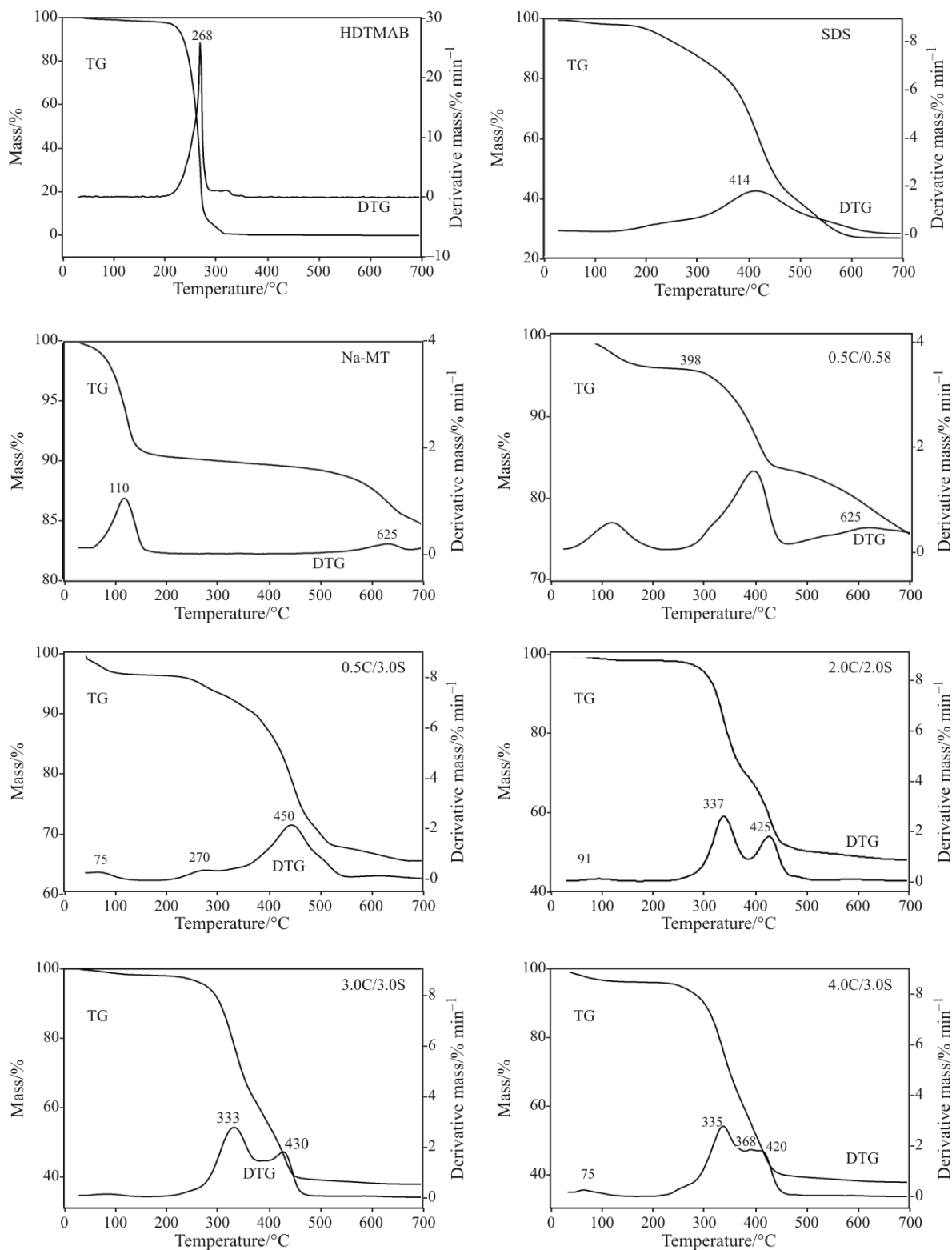


Fig. 6 TG and DTG curves of Na-MMT, surfactants and the representative organoclays

surface property transformation of montmorillonite from hydrophilic to hydrophobic and the replacement of hydrated sodium ions by cationic surfactants. With an increase of the loaded SDS, two mass loss steps,

corresponding to the loaded surfactants, are observed. For example, 0.5C/3.0S displays two mass loss steps at ca. 270 and 450°C, respectively. The former corresponds to the evaporation of cationic surfactants and the latter to the overlapping of the decomposition

of both cationic and anionic surfactants. The higher shift of the decomposition temperature to 450°C (0.5C/3.0S) from 398°C is due to the increased amount of the loaded SDS, which has a coexistence with HDTMAB just as 3.0C/3.0S and 4.0C/3.0S.

In DTG curve of 2.0C/2.0S, three mass loss steps are recorded. The first step at ca. 91°C is ascribed to dehydration while the second step at ca. 337°C corresponds to the decomposition of the intercalated HDTMAB [23]. The third step at 425°C should be attributed to the decomposition of the intercalated SDS.

To well understand the thermal characteristics of the resulting organoclays, peak fitting of the DTG curves are conducted and the representative curves are shown in Fig. 7. On the basis of the fitted DTG curves, the mass loss of the corresponding representative samples corresponding to different steps is calculated and presented in Table 1. In the resulting DTG curves of 3.0C/3.0S and 4.0C/3.0S, three peaks could be identified after peak-fitting (Fig. 7). The mass loss at ca. 335°C is resulted from the decomposition of the intercalated HDTMAB and the latter two to evaporation/decomposition of SDS. For sample 3.0C/3.0S, the mass loss at ca. 430°C is 15.6%, which is less than that of 0.5C/3.0S, 17.5%, while m of 3.0C/3.0S is more than that for 0.5C/3.0S (Fig. 4). This can be explained that some SDS of 3.0C/3.0S are attached to the external clay surface and these SDS are evaporated/decomposed at a lower temperature, ca. 398°C.

Our present study demonstrates that both the decomposition of the intercalated cationic and anionic surfactants increased when compared with that in neat

state. This should be attributed to coexistence of the two oppositely charged surfactants. As illustrated in literature [35, 36], the addition of other surfactants or additives on the molecular architecture of a surfactant can serve as a basis for forming microstructures such as complexes, mixed micelles, bilayers and tubules. The formation of various microstructures depends on the molar ratio and total concentration of opposite charged surfactants. The strong attractive interaction between oppositely charged head groups at the interface and hydrogen bonding will enhance the decomposition temperature of the corresponding surfactants.

Conclusions

In this study, a combination of elemental analysis, X-ray diffraction and thermogravimetric analysis is applied in the investigation of the surfactant loading and the thermal property of the resulting organoclays prepared using cationic and anionic surfactants. The present study shows that anionic surfactant can not be intercalated into clay interlayer space when only anionic surfactant is used in the preparation system. However, pre-modification of montmorillonite using cationic surfactant will facilitate the intercalation of anionic surfactant into clay interlayer space and results in an increase of the total amount of the loaded organic carbon and basal spacings of the organoclays. The loading of surfactants into montmorillonites also causes a transformation of clay surface property from hydrophilic to hydrophobic. The intercalated surfactants show higher decomposition temperature when compared to them in bulk state, resulted from the strong attractive interaction between oppositely charged head groups. These new insights are of high importance for the application of organoclays in the synthesis of clay-based nanocomposites and remediation of organic polluted water.

Acknowledgements

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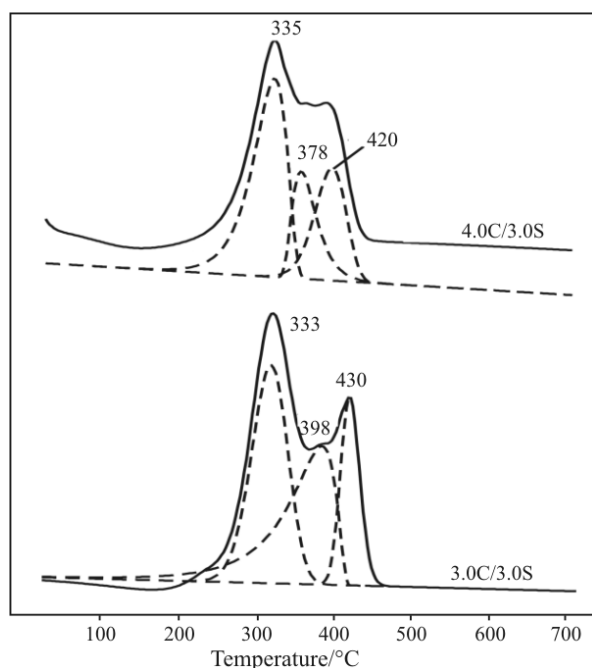


Fig. 7 The original (solid line) and fitted (dotted line) DTG curves of 3.0C/3.0S and 4.0C/3.0S

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