The structure and properties of OMt prepared by a synergistic modification strategy using the emulsifier OP-10 and hexadecyltrimethylammonium chloride as comodifiers

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Abstract
To improve the application performance of organic montmorillonite (OMt) and meet the OMt performance requirements of different fields, herein, we developed a synergistic modification method to prepare cationic–nonionic OMt (CN-Mt) using the emulsifier OP-10 and hexadecyltrimethylammonium chloride (CTAC) as comodifiers. The structure, morphology and properties of CN-Mt, cationic-OMt (C-Mt) and nonionic OMt (N-Mt) were studied by XRD, SEM, DSC, and contact angle and swell index measurements. CN-Mt has a larger layer spacing and thinner lamellae, which are obviously different from those of C-Mt and N-Mt. Moreover, CN-Mt was hydrophobic due to its denser organic surface molecules. The interlayer spacing of CN-Mt is positively related to the amount of modifier, and the amount of OP-10 contributes more to the interlayer spacing than CTAC. When the amounts of OP-10 and CTAC are 1.3 and 0.8 times the Mt cation exchange capacity (CEC), the interlayer spacing of the optimal CN-Mt is 4.49 nm, which is significantly higher than that of C-Mt (4.11 nm) at a 2.9 CEC, N-Mt (4.26 nm) at a 1.7 CEC and CN-Mt (4.20 nm) at a 0.9OP-10 + 1.5CTAC CEC. Benefiting from its structural merits, CN-Mt shows a higher degree of lamella separation, peeling and dispersion than C-Mt and N-Mt, as well as good thermal stability. Moreover, the lipophilicity and expansion of CN-Mt in medium- and low-polarity media are better than those of single-component OMT. Therefore, the structure and properties of CN-Mt can be controlled by adjusting the types and amount of modifier, further meeting the performance requirements of various application fields.

1. Introduction
Montmorillonite is known as a ‘universal clay mineral’ and has been commercialized in various fields because of its natural abundance and low cost. In recent years, there have been an increasing number of reports on the basic research and application of montmorillonite, especially the preparation and properties of organic montmorillonite (OMt). OMT is widely used in grease, paint, ink, cosmetics, medicine and health products, sewage treatment, oil-based drilling fluid, rubber and plastic materials, the national defense industry and other areas [1, 2]. However, the development and efficient utilization of OMT in different application fields still remain challenging because of the various performance requirements. For example, the good dispersion and gelation of OMT are important when it is used in grease, paint or ink. Matching the surface polarity of OMT (positive, negative or nonpolar) to that of pollutants is crucial for sewage treatment [3–5]. In rubber or plastic materials, OMT not only is required to have good dispersion and peeling properties but also needs good heat resistance to meet the processability requirements [6]. Excellent thermal stability and good rheological properties are indispensable for the wide use of OMT in oil-based drilling fluid [7, 8]. Therefore, it is desirable to prepare advanced OMT with controllable surface polarity, excellent thermal stability, good dispersion, and peeling properties.
Generally, OMT is prepared by exchanging organic cations with additional cations (such as Na\(^+\) and Ca\(^{2+}\)) in montmorillonite. That is, there is excess negative charge in montmorillonite due to the phenomenon of Al\(^{3+}\) in the octahedron being replaced by low-price ion-like species. Therefore, additional cations are needed to adsorb between layers to balance the charge and can be exchanged with organic cations to prepare OMT. \[9–11\] The current OMT applied in the market is cationic OMT, which is large-basal spacing OMT obtained by exchanging inorganic cations between montmorillonite layers with quaternary ammonium salt or quaternary phosphonium salt \[3, 12\]. Recently, some studies have showed that the modification agent of OMT is not limited to cationic surfactants but can include anionic \[13\] and nonionic surfactants \[4, 5, 11, 14\], which can also enter the interlayer of montmorillonite through set conditions and reactions. Moreover, the types of organic modifiers are not limited to one, as anionic-cationic OMT \[15, 16\] and anionic-nonionic OMT \[10\] have been reported. Meanwhile, Nong et al \[17\] and Zhuang et al \[18\] found that the type of hydrocarbyl group (aliphatic, aromatic quaternary and polyoxyethylene quaternary) in quaternary ammonium salt \[17\] and the length of aliphatic hydrocarbon chain \[18\], respectively, significantly affect the structure, morphology and properties of cationic OMT.

Some research groups have realized that nonionic OMT has good thermal stability but poor lipophilicity \[4, 13\] and that cationic OMT has better lipophilicity than nonionic OMT, while the thermal stability of the latter is worse than that of the former. These deficiencies restrict the application of OMT. To prove the application performance of OMT, we used OP-10 as a nonionic modifier and cetyltrimethyl ammonium chloride (CTAC) as a cationic modifier to jointly modify montmorillonite to prepare cation-nonionic OMT (CN-MT). The structure, morphology and properties of CN-Mt were studied and compared with those of cationic OMT and nonionic OMT. This work lays a foundation for the study of improving the properties of OMT to expand the application field of montmorillonite.

2. Experiment

2.1. Experimental materials

The cationic surfactant cetyltrimethyl ammonium chloride (CTAC, purity of 99.9%) and nonionic surfactant OP-10 (purity of 99%) were produced by Xilong, Shantou Chemical Co., Ltd. The structural formulas of the two reagents are shown in figure 1. Montmorillonite (Na-Mt) comes from Xuanhua, Hebei Province, and its cation exchange capacity (CEC) is 87 mmol/100 g. Its XRD patterns are shown in figure 2. The Na-Mt content is 84%. Cyclohexane and dimethyl sulfoxide (analytically pure) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Butyl acetate was purchased from Nanjing Chemical Reagent Co. Ltd.

2.2. Preparation of OMT

Na-Mt was dispersed in a three-neck flask filled with distilled water. After hydrating with electric stirring for 30 min, a certain amount of CTAC (or OP-10) was added to the montmorillonite suspension, which was stirred for 2 h, centrifuged, dried at 60 °C for 24 h, crushed, and sifted through a 200 mesh. Cationic OMT (C-Mt) or nonionic OMT (N-Mt) was obtained. According to the above method, CN-Mt was prepared by using CTAC and OP-10 as modification agents.

The material amount and ratio used in the preparation of OMT are shown in table 1.

2.3. Test and characterization

X-ray diffraction (XRD) was performed using a Japanese Science D/Max-RA (12 kW) x-ray diffractometer with copper target Kα rays. The scanning angle was 1.5° ~ 90°, the scanning speed was 4°/min, the voltage was 40 kV, and the current was 100 mA.
Scanning electron microscopy (SEM) was performed with a JEOL JSM-7001F cold field emission electron microscope with a voltage of 15 kV.

Differential scanning calorimetry (DSC) was performed by an STA 6000 synchronous thermal analyzer from PerkinElmer Instruments Co., Ltd. The temperature was increased from 30 °C to 400 °C at a rate of 10 °C min⁻¹ in a N₂ atmosphere at a flow rate of 20 ml min⁻¹.

The contact angle test adopted a JC200D contact angle measuring instrument. Each sample was measured 3 times, and the average value was taken.

The swell index test process was based on the National Standard of the People’s Republic of China GB/T 20973-2007, and the drying temperature of OMt was 60 °C.

### 3. Results and discussion

#### 3.1. XRD analysis

The crystallinity of Na-Mt, 0.8CTAC + Mt, 1.5CTAC + Mt, 2.2CTAC + Mt, and 2.9CTAC + Mt was tested by XRD (figure 3). The interlayer spacing of Na-Mt is 1.26 nm. However, that of cationic C-Mt obtained by CTAC modification is larger than that of Na-Mt, indicating that intercalated C-Mt was obtained. Moreover, the C-Mt interlayer spacing increased with increasing CTAC amount and reached 4.11 nm when the amount was 2.9. The diffraction peak intensity of C-Mt also gradually increased with increasing CTAC amount. When the

![XRD patterns](image-url)
amounts of CTAC were 1.5, 2.2 and 2.9 CEC, the three C-Mt samples showed second-order (002) and third-order (003) diffraction peaks.

The crystallinity of Na-Mt, 0.5OP-10 + Mt, 0.9OP-10 + Mt, 1.3OP-10 + Mt, and 1.7OP-10 + Mt was tested by XRD analysis, as shown in figure 4. Similar to that of Na-Mt and C-Mt prepared with different amounts of CTAC, the interlayer spacing of N-Mt is significantly larger than that of Na-Mt, the interlayer spacing of N-Mt increases gradually, and the intensity of the diffraction peak increases gradually with increasing amounts of OP-10. When the amount of OP-10 is 1.7 CEC, the interlayer spacing of N-Mt reaches 4.26 nm. When the amounts of OP-10 are 0.9, 1.3 and 1.7 CEC, the XRD patterns of N-Mt show third-order diffraction peaks. The results show that OP-10 enters the Na-Mt interlayers, and the arrangement between the interlayers is more regular.

Figure 5 shows the XRD patterns of CN-Mt prepared with different ratios of cationic (CTAC) and nonionic (OP-10) modifiers. When the amount of fixed OP-10 was 0.5 CEC and the amount of CTAC was increased from 0.8 to 2.2 CEC, the interlayer spacings of CN-Mt gradually increased to 3.55 nm, 3.73 nm and 4.02 nm, which are all greater than the interlayer spacings of 0.5OP-10 + Mt (1.8 nm) and 0.8, 1.5 and 2.2 CEC C-Mt (2.06 nm, 3.24 nm and 3.88 nm, respectively). The results show that OP-10 and CTAC fully entered the Mt interlayer. Comparing the three groups of CN-Mt with different amounts of OP-10, i.e., 1.3OP-10 + 0.8CTAC + Mt (4.49 nm), 0.9OP-10 + 0.8CTAC + Mt (3.90 nm) and 0.5OP-10 + 0.8CTAC + Mt (3.55 nm), their interlayer spacing was positively correlated with the amount of OP-10. At the same time, comparing the other three groups of CN-Mt with different amounts of CTAC, i.e., 0.5OP-10 + 2.2CTAC + Mt (4.02 nm), 0.5OP-10 + 1.5CTAC + Mt (3.73 nm) and 0.5OP-10 + 0.8CTAC + Mt (3.55 nm), the interlayer spacing of CN-Mt was also positively correlated with the amount of CTAC. For the first three groups of CN-Mt, the amount of OP changes relatively little, but the interlayer spacing changes are relatively large. For the last three groups of CN-Mt, the change in the amount of CTAC is relatively large, but the change in interlayer spacing is relatively small. Therefore, the contribution of OP-10 to the interlayer spacing is greater than that of CTAC. This is due to OP-10 having a larger molecular weight and spatial volume than CTAC.

3.2. SEM analysis

The morphological structures of 2.9CTAC + Mt, 1.7OP-10 + Mt, 0.9OP-10 + 1.5CTAC + Mt and Na-Mt were investigated by SEM (figure 6). The Na-Mt lamellae are densely packed and are in the form of large particles (figure 6(A)). C-Mt is lamellar and thick (figure 6(B)). N-Mt is also lamellar, but the lamella is curved, indicating that the lamella is thin and flexible (figure 6(C)). CN-Mt mainly exists in the form of loose flakes (figure 6(D)). The order of the lamella separation and dispersion degree of the three OMt samples is 0.9 OP-10 + 1.5CTAC + Mt > 1.7OP-10 + Mt > 2.9CTAC + Mt. The results show that the comodification of Mt
by cationic and nonionic surfactants can improve the interlayer environment and the surface properties of Mt lamellae and promote the thickness and particle size of Mt lamellae to thin, small and loose degrees.

3.3. Thermal analysis

Three samples, 2.9CTAC + Mt, 1.7OP-10 + Mt and 0.9OP-10 + 1.5CTAC + Mt, were analyzed by DSC to study the thermal stability of the different types of OMt. As shown in figures 7, 1.7OP-10 + Mt, 2.9CTAC + Mt and 1.5CTAC + 0.9 OP-10 + Mt show obvious exothermic peaks at 386 °C, 275 °C and 285 °C, respectively. 1.7OP-10 + Mt has the best thermal stability, while 2.9CTAC + Mt has the worst thermal stability. However, the thermal stability of 0.9OP-10 + 1.5CTAC + Mt is between the thermal stabilities of the above two samples. As 0.9 CEC OP-10 replaces 1.4 CEC CTAC, the exothermic peak temperature of 0.9OP-10 + 1.5CTAC + Mt increased by 10 °C (from 275 °C to 285 °C). In addition, the exothermic peak at 386 °C of 0.9OP-10 + 1.5CTAC + Mt disappeared from the DSC graph, indicating that the thermal stability of 0.9OP-10 + 1.5CTAC + Mt is not achieved by the simple addition effect of 1.7OP-10 + Mt and 2.9CTAC + Mt. It is the comprehensive effect of the synergistic interaction between the two modifiers and montmorillonite and its own thermal stability. Therefore, the combination and synergistic effect of different types of organic modifiers can regulate the thermal stability of OMt.

At the same time, the three OMt samples have no obvious endothermic valley due to interlayer water removal between 100 °C and 150 °C (Mt interlaminar water), indicating that organic modification is complete, and the modifier molecules fully replace the Na ions in the interlaminar water and then lose the interlaminar water. In addition, C-Mt, N-Mt and CN-Mt all have a small endothermic valley near 39 °C, which is attributed to the surface adsorption of water on OMt.

3.4. Contact angle

Figure 8 shows a histogram of the contact angles of C-Mt, N-Mt and CN-Mt samples prepared with different doses of modifier.

As shown in figure 8, the contact angle of N-Mt increases with the amount of OP-10 in 0.5 CEC, 0.9 CEC, 1.3 CEC and 1.7 CEC, and their contact angles do not change much, increasing to 30°, 29°, 29°, and 34°.
respectively. Although the amount of OP-10 adsorbed on the surface of Mt is positively correlated with the
amount of OP-10, the hydrophobicity of N-MT is not positively correlated with the amount of OP-10 because of
the existence and exposure of polar groups such as hydroxyl, alkoxy and aromatic ring groups on the molecular
chain of OP-10. However, the change in the C-Mt contact angle with the amount of modifier is different from
that in the N-Mt contact angle. With the increase in the amount of CTAC, the contact angle of C-Mt increases

Figure 5. XRD patterns of cationic-nonionic organo-montmorillonite.

Figure 6. SEM images of (A) Na-Mt, (B) 2.9CTAC + Mt, (C) 1.7OP-10 + Mt and (D) 1.5CTAC + 0.9OP-10 + Mt.
first and then decreases. When CTAC increases from 0.8 CEC to 1.5 CEC, the maximum contact angle reaches 55° and then decreases gradually. To reveal the underlying mechanism, we provide a schematic diagram of the CTAC adsorption state on the C-Mt surface with different CTAC amounts in figure 9. A certain amount of CTAC is first adsorbed on the surfaces of Mt as a single layer. With the increased amount of modifier, the ammonium end group is adsorbed on the surface of Mt, and the alkyl chain extends outward until the surface of montmorillonite is fully covered (figure 9(B), (C)). At the same time, C-Mt has lower polarity and higher lipophilicity. The hydrocarbon chain of CTAC added later will be absorbed and will deposit on the first CTAC layer with the part of the hydrocarbon chain that was adsorbed on the C-Mt laminate, and the polar end will be oriented outward, as shown in figure 9(D). As a result, the surface polarity of C-Mt increases again, and the contact angle is reduced again. For CN-Mt except 1.3OP-10 + 0.8CTAC-Mt (42°) with a high OP-10 dose, the contact angle of CN-Mt is approximately 64°, which is significantly higher than that of C-Mt or N-Mt modified with a single-component surfactant. The results show that the contact angle of CN-Mt prepared by CTAC and OP-10 is larger than that of C-Mt and N-Mt. Therefore, the lipophilicity of OMt can be controlled by adjusting the ratio of the amounts of cationic and nonionic modifiers.
3.5. Swell indices

The swell indices of the C-Mt, N-Mt and CN-Mt samples in different polar organic media are shown in Table 2. Based on the results in Table 2, CN-Mt has the highest swell index, N-Mt has the lowest, and the swell index of C-Mt is between the swell indices of the other two types of OMt, which is consistent with the change rule of the contact angle. The swell index of N-Mt in cyclohexane is higher than that in butyl acetate and dimethyl sulfoxide, with the highest being 9 ml/2 g. C-Mt has poor expansibility in cyclohexane, with low polarity, but has good expansibility in butyl acetate and dimethyl sulfoxide, with higher polarity. The swell index of the 1.5CTAC + Mt sample is the highest (12.0 ml/2 g) in butyl acetate. In the three different types of polar media, the swell index increases first and then decreases with increasing CTAC amount, which is consistent with the change law of the contact angle. CN-Mt has better expansibility in butyl acetate and cyclohexane than in dimethyl sulfoxide. The swell indices of 1.5CTAC + 0.9OP-10 + Mt in butyl acetate and cyclohexane are 25.5 ml/2 g and 19.0 ml/2 g, respectively. These values are much higher than the maximum values of N-Mt (9.0 ml/2 g in cyclohexane) and C-Mt (12.0 ml/2 g in butyl acetate). The above results show that CN-Mt has better expansibility than single-component C-Mt and N-Mt in the three types of media. At the same time, the expansion properties of CN-Mt can be controlled by adjusting the types and combination ratio of modifiers to meet the different requirements of OMt for different systems.

Table 2. Material amount and ratio used in OMt preparation.

| Samples       | Swelling indices (ml/2 g) | Cyclohexane | Butyl acetate | Dimethyl sulfoxide |
|---------------|---------------------------|-------------|---------------|--------------------|
| 0.8 CTAC      |                           | 4.0         | 7.0           | 5.0                |
| 1.5 CTAC      |                           | 6.2         | 12.0          | 8.2                |
| 2.2 CTAC      |                           | 7.4         | 10.0          | 7.0                |
| 2.9 CTAC      |                           | 4.9         | 5.1           | 6.0                |
| 0.5 OP-10     |                           | 3.0         | 2.0           | 4.1                |
| 0.9 OP-10     |                           | 4.0         | 2.0           | 2.6                |
| 1.3 OP-10     |                           | 5.0         | 3.0           | 2.1                |
| 1.7 OP-10     |                           | 9.0         | 7.0           | 2.2                |
| 0.5 OP-10 + 0.8 CTAC |                   | 5.8         | 4.2           | 7.3                |
| 0.5 OP-10 + 1.5 CTAC  |                     | 17.3        | 19.0          | 12.4               |
| 0.5 OP-10 + 2.2 CTAC  |                     | 14.5        | 13.5          | 11.7               |
| 0.9 OP-10 + 0.8 CTAC |                   | 10.5        | 9.8           | 9.0                |
| 0.9 OP-10 + 1.5 CTAC  |                     | 19.0        | 25.5          | 7.9                |
| 1.3 OP-10 + 0.8 CTAC |                   | 11.0        | 10.0          | 7.0                |
4. Formation mechanism and properties of CN-Mt

Figure 10 is a schematic diagram of the CN-Mt formation mechanism. CN-Mt is the product of CTAC and OP-10 adsorption on the inner and outer surfaces of montmorillonite (figure 10(D)). The layer charge of Mt is $0.2 \sim 0.6$ for a single unit cell and $0.4 \sim 1.2$ for a region of approximately $5.5 \text{ nm}^2$ (two cells). During the adsorption of CTAC by montmorillonite, Mt absorbs at most one positively charged CTAC in the region of $5.5 \text{ nm}^2$. The terminal ammonium of CTAC adsorbed on the surface of Mt will occupy approximately $0.18 \text{ nm}^2$. When the adsorption of CTAC on the Mt surface reaches saturation, the Mt surface is still bare in many places. There are many oxygen atoms (oxygen atoms in the silicon oxygen tetrahedron) on these exposed surfaces. Therefore, in the presence of OP-10, the hydroxyl group on the OP-10 chain will form hydrogen bonds with this oxygen and absorb on the surface, finally yielding CN-Mt (figure 10(D)).

Similarly, after OP-10 first interacts with Mt to form N-Mt (figure 10(C)), the exposed negative potential will further interact with the ammonium terminus of CTAC to form CN-Mt (figure 10(D)). Therefore, the interlayer and surface of CN-Mt adsorb more organic molecules than C-Mt or N-Mt, so the organic molecules on the surface of CN-Mt are denser and the hydrophobicity of CN-Mt is enhanced. Therefore, CN-Mt has a larger interlayer spacing and contact angle than C-Mt and N-Mt and is better than C-Mt and N-Mt in swelling, dispersion and stripping properties in nonpolar and weakly polar systems.

5. Conclusions

Cationic and nonionic surfactants can be used to synergistically modify montmorillonite to obtain CN-Mt, in which both surfactants enter the montmorillonite interlayer. CN-Mt is obviously different from C-Mt and N-Mt in structure, morphology and performance. The interlayer spacing of CN-Mt is positively correlated with the amount of the two modifiers. OP-10 has a greater contribution to the interlayer spacing of CN-Mt than CTAC. When the amount is $1.3\text{OP-10} + 0.8\text{CTAC}$, the interlayer spacing of CN-Mt ($d_{001} = 4.49 \text{ nm}$) is higher than that of $2.9\text{CTAC} + \text{Mt}$ ($d_{001} = 4.11 \text{ nm}$) and that of $1.7\text{OP-10} + \text{Mt}$ ($d_{001} = 4.26 \text{ nm}$). The degree of stripping of CN-Mt is higher than that of C-Mt and that of N-Mt. In particular, the hydrophobicity of CN-Mt is significantly higher than that of C-Mt and that of N-Mt, and the contact angle reaches $64^\circ$. Therefore, CN-Mt has better expansibility and dispersion than C-Mt and N-Mt in high-, medium- and low-polarity organic media. The thermal stability of N-Mt is better than that of C-Mt, and that of CN-Mt is better than that of C-Mt. The results of this study provide an experimental basis for the study of regulating the properties of OMt and have important significance for expanding the application field of OMt and meeting the application demand of OMt in various fields.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] Qiu J, Lv X J and Song J Y 2006 Current aspects of organically modified montmorillonite China Powder Technology 12 40–4
[2] Xu G N, Jiang H L and Xie H L 2008 Preparation and property characterization of the OMt Journal of Jiangnan University (Natural Science Edition) 7 91–5
[3] He H et al 2006 Microstructure of HDTMA⁺-modified montmorillonite and its influence on sorption characteristics Clays & Clay Minerals 54 689–96
[4] Guégan R et al 2015 Nonionic organoclay: A ‘Swiss Army knife’ for the adsorption of organic micro-pollutants Journal of Colloid & Interface Science 437 71–9
[5] Nourmoradi H, Nikaeen M and Khiadani M 2012 Removal of benzene, toluene, ethylbenzene and xylene (BTEX) from aqueous solutions by montmorillonite modified with nonionic surfactant: equilibrium, kinetic and thermodynamic study Chem. Eng. J. 191 341–8
[6] Silva I A et al 2014 Modification of bentonites with nonionic surfactants for use in organic-based drilling fluids Appl. Clay Sci. 95 371–7
[7] Hermoso J, Martinez B F and Gallegos C 2014 Influence of viscosity modifier nature and concentration on the viscous flow behaviour of oil-based drilling fluids at high pressure Appl. Clay Sci. 87 14–21
[8] Minase M et al 2008 The viscosity of organic liquid suspensions of trimethyl dococyl ammonium montmorillonite complexes Clays Clay Miner. 56 49–65
[9] Bergaya F, Jaber M and Lambert J 2011 Organophilic clay minerals ed M Galimberti Rubber–Clay Nanocomposites: Science, Technology, and Applications [M], (John Wiley & Sons, Inc.) 45–86
[10] Zhuang G et al 2015 A new ball milling method to produce organo-montmorillonite from anionic and nonionic surfactants Appl. Clay Sci. 104 18–26
[11] Zhuang G et al 2017 Influence of the nonionic surfactants’ nature on the structures and properties of organo-montmorillonites Colloids & Surfaces A Physicochemical & Engineering Aspects 518 116–23
[12] Erkan I, Alp I and Celik M S 2010 Characterization of organo-Bentonites obtained from different linear-chain quaternary alkylammonium salts Clays Clay Miner. 58 792–802
[13] Zhang Z, Liao L and Xia Z 2010 Ultrasound-assisted preparation and characterization of anionic surfactant modified montmorillonites Appl. Clay Sci. 50 376–81
[14] Yang K, Zhu L and Zhao B 2005 Minimizing losses of nonionic and anionic surfactants to a montmorillonite saturated with calcium using their mixtures Journal of Colloid & Interface Science 291 59–66
[15] Wu S et al 2014 Influence of montmorillonites exchange capacity on the basal spacing of cation–anion organo-montmorillonites Mater. Res. Bull. 59 59–64
[16] Zhang Z et al 2013 Synergistic effect of cationic and anionic surfactants for the modification of Ca-montmorillonite Mater. Res. Bull. 48 1811–6
[17] Nong Y Y et al 2021 Effects of cation modifier type on the structure and morphology of organo-montmorillonite and its application properties in a high-temperature white oil system Appl. Clay Sci. 203 0169–1317
[18] Zhuang G Z, Jiang W B and Zhang Z P 2019 Organic modifiers of organo-montmorillonite in oil system under high temperatures: desorption or degradation Ind. Eng. Chem. Res. 58 2644–53