



Original Paper

Wettability alteration of organo-vermiculites induced by layer charge and tailored *bis*-N-heterocyclic quaternary ammonium salts

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ABSTRACT

Wettability is an important surface property that deserves to further explore the factors on its alteration. Series of *bis*-N-heterocyclic quaternary ammonium salts with different spacer length and N-heterocyclic headgroups (morpholinium (BMMB, BMMD and BMMH), piperidinium (BPMH) and piperazinium (BMPMH)) have been synthesized and employed for altering the wettability of vermiculite and its derivatives (Vts) treated by Li⁺-saturated heating method. The results of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TG-DTG), scanning electron microscopy (SEM) and N₂ adsorption/desorption isotherms indicate that all of the *bis*-N-heterocyclic quaternary ammonium salts have been successfully inserted into the vermiculite layers, leading to the organic monolayer. The results of capillary rise tests combined with Lipophilic to Hydrophilic Ratio (LHR) values unveil the wettability alteration of the organo-Vts. As the layer charge decreases, the hydrophilicity of the organo-Vts gradually increases, which is probably caused by the decline in binding sites. As the result of the change in spacer length of modifier, the wetting properties of morpholinium-based organo-Vts change in order of BMMD-Vts > BMMH-Vts > BMMB-Vts, and difference in N-heterocyclic headgroups leads to the sequence of wettability: BMPMH-Vts > BPMH-Vts > BMMH-Vts. Layer charge of Vt, spacer length and the type of the N-heterocyclic headgroup of modifier have the synergistic effect on the regulation of the wettability.

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1. Introduction

Wettability, one of crucial surface characters of material, reflects the interest of the liquids on the surface (Wang et al., 2011; Magalhães da Silva and Oliveira, 2021). Based on the difference in behaviors of liquids on material, several measuring methods are developed for measuring the wettability of surface (Alghunaim et al., 2016; Alghunaim and Zhang Newby, 2016; Tohry et al., 2020; Magalhães da Silva and Oliveira, 2021), and the Washburn capillary rise method is more applicable to evaluate the powder wettability (Chau, 2009; Ding and Gao, 2021). As one of important surface properties, wettability takes an important place in the mechanisms of fields of environmental remediation, mineral flotation, especially oil exploitation (Bera et al., 2017; Gao et al., 2019; Pan et al., 2020; Deng et al., 2021; Ding and Gao, 2021; Yang et al., 2021). Facing the shortage of the fossil resource, which is

still indispensable, enhanced oil recovery has been drawn more attention (Ding et al., 2018b). Wettability alteration, as an effective mechanism, comes into the view of the researchers to solve the problems and develop the technology of enhanced oil recovery (Ding and Gao, 2021). Therefore, further understanding the wettability alteration is of importance for the development of petrochemical and nanomaterial industry.

Layer charge is of the most important intrinsic properties of clay mineral, which originates from the isomorphous substitution of the structure of mineral (de Queiroga et al., 2016), affects the cation exchange capacity (CEC), adsorption capacity as well as the wettability of materials (Dultz et al., 2012; Peng et al., 2021). As reported by literatures, Li⁺-saturated heating method can effectively reduce the layer charge but keep the original structure of the clay mineral through the Hofmann-Klemen effect, which results by the migration of dehydrated cation into layers (Komadel et al., 2005). To date, attempts have been carried out to study the effect of reducing layer charge of Li⁺-saturated montmorillonite on the wettability alteration (Luo et al., 2014a). However, the reduced-

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charge vermiculite (RCVt) from its Li^+ -forms, which own similar structure but higher layer charge than montmorillonite (Vinci et al., 2020), is merely reported, which can offer a specific model for exploring the influence of the layer charge at the wide range of charge variation.

Organic modification is also recognized as an effective way for regulating the wettability. On account of the interaction between the surfactant and matrix, the wettability changes differently with the type and structure of modifiers, such as cationic/anionic/nonionic surfactants, as well as the quaternary ammonium salts with special groups (e.g. pyridinium and imidazolium, etc.) (Luo et al., 2014b; Hou et al., 2015; Ding et al., 2018b, 2022). Hou et al. (2015) have reported that the cation surfactant shows the more effective alteration on the wettability of the oil-wet sandstone than anionic and nonionic surfactant. Luo et al. (2014b) have reported the wettability alteration of reduced-charge montmorillonites modified by quaternary ammonium salts with different number of headgroups, which shows that both of the layer charge and structure of modifiers affect the wetting properties. Ding et al. (2018b) have compared the wettability of organo-vermiculites altered by *bis*-quaternary ammonium and *bis*-pyridinium salts, suggesting that the difference in headgroups result in the different wetting characteristics. Therefore, it is worth noting that the molecule design of modifier may endow the different properties of the particles. Benefited from the unique structure and environmentally friendly nature, *bis*-N-heterocyclic salts, the special kind of quaternary ammonium salts with N-heterocyclic headgroups (morpholinium, piperidinium and piperazinium) that own the polar/non-polar groups, may be apt to bring some new thoughts on the regulation of wettability, which are never reported before.

In this work, vermiculite and its derivatives with reduced-charge (Vts), treated by Li^+ -saturated heating method, are chosen as the representative matrixes. And series of *bis*-N-heterocyclic quaternary ammonium salts with different spacer lengths and N-heterocyclic headgroups (morpholinium, piperidinium and piperazinium) have been synthesized and employed for further exploring the wettability alteration of the high-charged clay mineral. Several characterization methods, such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TG-DTG), scanning electron microscopy (SEM) and N_2 adsorption/desorption isotherms, are employed for characterizing the structure and morphology of *bis*-N-heterocyclic-containing organo-vermiculites. The wettability alteration of these *bis*-N-heterocyclic-based organo-Vts are measured by capillary rise tests combined with Lipophilic to Hydrophilic Ratio (LHR) values. This work aims at exploring the relationship between wettability alteration and layer charge as well as modifiers, giving some ideas about the molecular design of modifier for altering wettability of clay mineral with different charge.

2. Materials and methods

2.1. Materials

The vermiculite (Vt, CEC of $123 \text{ mmol (100 g)}^{-1}$) was obtained from Sigma-Aldrich. 4-methylmorpholine, 1-methylpiperidine, 1,4-dimethyl-piperazine were provided by J&K, and 1,4-dibromobutane, 1,6-dibromohexane, 1,10-dibromodecane, ethanol, ethyl acetate and cyclohexane were purchased from Energy Chemical and Aladdin, respectively. Deionized water ($18 \text{ M}\Omega \text{ cm}$) was employed in all experiments. All reagents were used as received without further purification.

2.2. Synthesis of *bis*-N-heterocyclic salts

According to the literature, series of *bis*-N-heterocyclic quaternary ammonium salts with different spacer length and N-heterocyclic headgroups (morpholinium, piperidinium and piperazinium) were synthesized (Fig. 1) (Bhadani et al., 2015; Huang et al., 2020). Firstly, 4-methylmorpholine (1-methylpiperidine, 1,4-dimethyl-piperazine) was mixed with dibromo alkane in the ethanol solution. After refluxed for 72 h, the mixtures were cooled to room temperature and distilled to remove solvents, then washed by ethyl acetate for times. Finally, the resulting *bis*-N-heterocyclic salts, 1,4-bis(morpholinomethylammonio)butane dibromide, 1,6-bis(morpholinomethylammonio)hexane dibromide, 1,10-bis(morpholinomethylammonio)decane dibromide, 1,6-bis(piperidinomethylammonio)hexane dibromide, 1,6-bis(4-methylpiperazino-1-methylammonio)hexane dibromide were collected by filtration and dried in oven for 48 h, which were labeled as BMMB, BMMH, BMMD, BPMH and BMPMH, respectively. All as-synthesized *bis*-N-heterocyclic salts were tested by FT-IR, elemental analysis as well as ^1H NMR.

2.3. Samples preparation

The vermiculites with reduced layer charge were pretreated at 100, 200, 300 °C through the Li^+ -saturated heating method that reported by Lim and Jackson (1986), and the obtained particles were named as Vt-1, Vt-2 and Vt-3. As the reference value of layer charge (Mermut and Lagaly, 2001; Pentrák et al., 2012), the CEC of Vt-1, Vt-2 and Vt-3 were 110, 99 and 84 mmol (100 g)^{-1} , respectively.

1.0 g of Vt and pretreated reduced-charge vermiculites were mixed with the stoichiometric amount of *bis*-N-heterocyclic salts (corresponding to 1.0 CEC of the clay samples), which were pre-dissolved in 30 mL aqueous solution, in oscillator at 60 °C for 3 h, separately. After that, the products were centrifugated and washed by water for times, then dried at 80 °C in oven overnight. The resultant samples were ground and sieved through 200 mesh for use and denominated in the way as follows: BMMB-Vt represented Vt modified by BMMB.

2.4. Characterizations

^1H NMR was performed on a JEOL JNM-ECZ400S/L1 spectrometer in 400 MHz using D_2O as the solvent. Fourier transformed infrared spectroscopy (FT-IR) of the as-synthesized *bis*-N-heterocyclic salts, raw Vt and its derivatives were collected by Nicolet iS10 spectrometer through the KBr pellet method, and the spectra were recorded at the range of $4000\text{--}400 \text{ cm}^{-1}$ with the resolution of 4 cm^{-1} . Thermogravimetric analysis (TG) was carried through Mettler Toledo TG-DSC3+ STARE system in nitrogen atmosphere. The powder X-ray diffraction (XRD) patterns were obtained by Bruker D8 Advance X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) at 40 kV and 40 mA in the range of $2\text{--}10^\circ$. The specific surface areas of the particles were determined by TriStar II 3020 based on the Brunauer-Emmett-Teller (BET) method. The scanning electron microscopy (SEM) photomicrographs of Vts and organo-Vts were recorded via SU8010 scanning electron microscope.

2.5. Wettability tests

The wettability of the samples was evaluated by Washburn capillary rise tests at room temperature. Testing theory and schematic setup of capillary rise method are shown in supporting material, and the procedure was as follows: Firstly, 0.4 g particles were

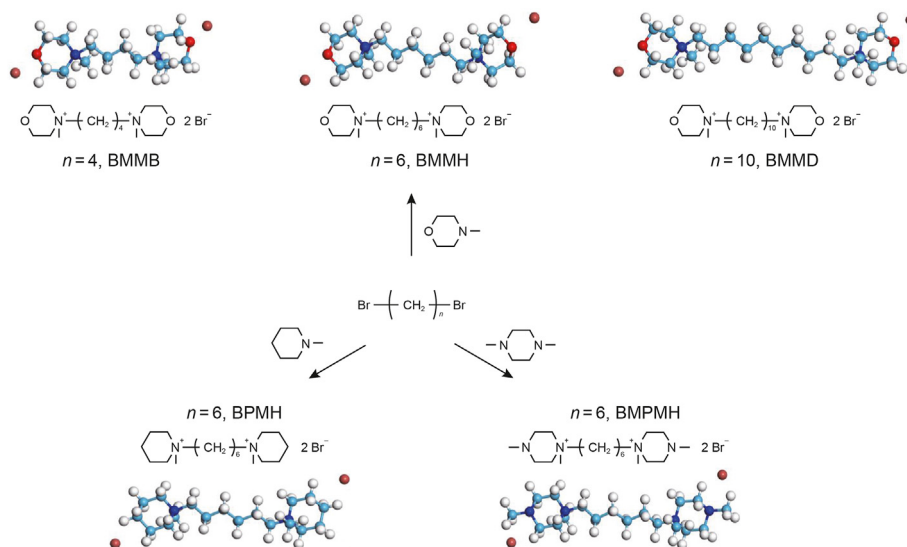


Fig. 1. The schematic diagram of synthesis of bis-N-heterocyclic quaternary ammonium salts.

packed into the tubes and tapped hundreds of times, and put on the powder contact angle measuring apparatus. Then, the dishes filled with testing liquids (cyclohexane and deionized water for oil and water phases, respectively) were raised, once the liquid touched the bottom tubes, the particles could be wetted, and the data were collected by computer. The value of Lipophilic to Hydrophilic Ratio (*LHR*), the index of relative wettability, was calculated by Eq. (S5) (Chang et al., 2009; Susana et al., 2012; Ding et al., 2018b).

3. Results and discussion

3.1. Characterizations of bis-N-heterocyclic salts

The FT-IR of resulting bis-N-heterocyclic quaternary ammonium salts are demonstrated in Fig. 2. The adsorption bands at 3427 and

1625 cm^{-1} correspond to the physisorbed water of the samples (Ding et al., 2018a). The C–H stretching and bending vibrations of bis-N-heterocyclic quaternary ammonium salts are appeared at 2941, 2859 and 1469 cm^{-1} , respectively (Cheng et al., 2020). Bands at 1282, 1213, 1116 and 1060 cm^{-1} are related to the vibrations of C–N and C–O in morpholine, piperidine and piperazine rings, respectively (Ni et al., 2019; Rahimov et al., 2021). The ^1H NMR spectra of all bis-N-heterocyclic salts are depicted in Fig. S2–S6, and the results of element analysis and ^1H NMR of the resultant organic salts are collected in Table 1. Combined with these characterizations results, it can be confirmed that all of the synthetic products are target bis-N-heterocyclic quaternary ammonium salts, which can be used for modifying the clays in the following experiments.

3.2. XRD analyses of vermiculites/organo-vermiculites

The XRD patterns of Vt and reduced-charge vermiculites before and after modification are shown in Fig. 3. The characteristic diffraction peak at around 6.2° corresponds to the typical d_{001} spacings, which can be deduced by Bragg's law, of 1.43 nm of pristine Vt (Yin et al., 2017). The reflection peaks at around 7.4° and 8.7° with d -values of 1.20 nm and 1.01 nm belong to the one-water hydration layer and dehydrated layer of the Vt structure, respectively (Marcos et al., 2009; Ferrage et al., 2010). After reduced-charge treatment, the slightly migration of the reflection peaks of reduced-charge vermiculites may be resulted from the evaporation of water during the treatment (Kristkova et al., 2004). Compared with the raw Vt, the similar XRD patterns indicate that the reduced-charge vermiculites treated by Li^+ -saturated heating method still keep the stratified structure.

As shown in Fig. 3(a), there is a mild expansion of the layer spacing of Vt after organic cations intercalation, and the basal spacings of bis-N-heterocyclic-based organo-Vt slightly shift from 1.43 to 1.44 nm. This fact confirms that all of these bis-N-heterocyclic salts are inserted into the layers of Vt with the monolayer arrangement (Luo et al., 2014a; Caglar et al., 2016), which may be the reason for the decrease in the distances of monohydrated layer of organo-Vts from 1.20 to 1.19 nm. Reduced-charge vermiculites modified by bis-N-heterocyclic quaternary ammonium salts also show the same phenomenon (Fig. 3(b)–(d)). In spite of the change of the layer charge, almost all of the modified reduced-charge

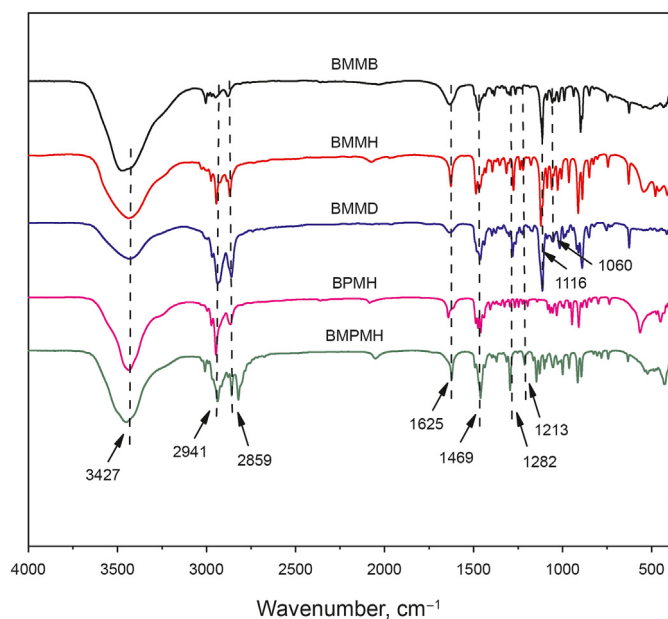


Fig. 2. The FT-IR spectra of the resulting bis-N-heterocyclic quaternary ammonium salts.

Table 1
Elemental analysis and ^1H NMR of the resulting *bis*-N-heterocyclic quaternary ammonium salts.

	Elemental analysis, %					^1H NMR	
	C		H		N		
	Cal.	Exp.	Cal.	Exp.	Cal.		Exp.
BMMB	40.19	38.60	7.18	6.60	6.70	6.44	δ 3.96 (s, 8H), 3.48–3.39 (m, 12H), 3.13 (s, 6H), 1.84 (m, 4H)
BMMH	43.05	42.77	7.62	7.37	6.28	6.18	δ 4.03 (t, 8H), 3.48 (m, 12H), 3.17 (s, 6H), 1.82 (m, 4H), 1.45 (m, 4H)
BMMD	47.81	47.25	8.37	7.63	5.58	5.50	δ 4.01 (t, 8H), 3.44 (m, 12H), 3.15 (s, 6H), 1.76 (m, 4H), 1.34 (m, 12H)
BPMH	48.87	47.45	8.60	8.60	6.33	6.17	δ 3.20 (t, 12H), 2.89 (s, 6H), 1.74 (m, 8H), 1.65 (m, 4H), 1.53 (m, 4H), 1.31 (m, 4H)
BMPMH	45.76	44.82	8.47	7.67	11.86	11.58	δ 3.36 (m, 12H), 3.01 (s, 6H), 2.78–2.73 (m, 8H), 2.27 (s, 6H), 1.71 (m, 4H), 1.35 (m, 4H)

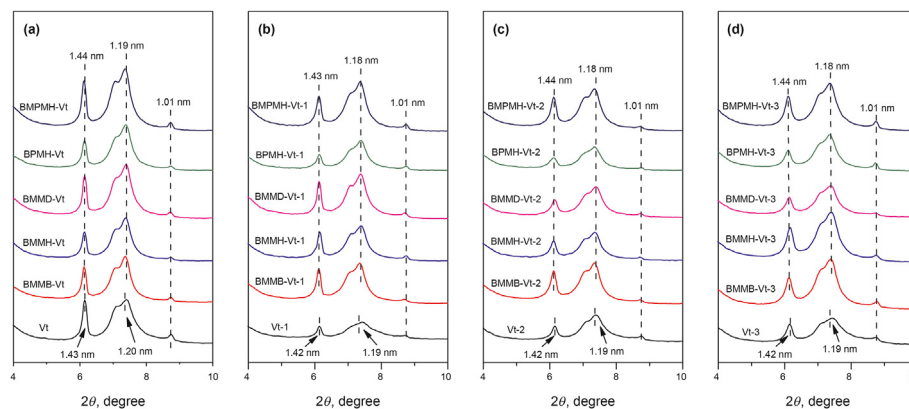


Fig. 3. The XRD patterns of the Vts and *bis*-N-heterocyclic-based organo-Vts.

vermiculite shows the same enlarged *d*-spacings, which may result by their similar molecule structure of modifier.

In conclusion, during the modification process of *bis*-N-heterocyclic quaternary ammonium salts, there is the monolayer of *bis*-N-heterocyclic salts formed between layers of the raw and reduced-charge vermiculites. On account of the similar molecule structure of the modifiers, the *d*-spacings are enlarged independent with the change of layer charge.

3.3. FT-IR analyses of vermiculites/organo-vermiculites

Given that their similar structures, the raw and modified Vt and Vt-2 are chosen as the templates, and their FT-IR spectra are demonstrated in Fig. 4. As shown in Fig. 4(a), the strong and broad bands at around 3438 cm^{-1} are related to the $-\text{OH}$ stretching vibrations of crystal structure of Vt (Yu et al., 2010). Bands at 1639 cm^{-1} correspond to the $\text{H}-\text{O}-\text{H}$ bending vibration of adsorbed water or moisture in the Vt (Brião et al., 2021). The spiculate bands at 1001 cm^{-1} are identified as the $\text{Si}-\text{O}$ stretching vibrations of the silicate layers (Guan et al., 2015; İşçi, 2017; Brião et al., 2021). Bands at around 817 , 680 and 454 cm^{-1} are assigned to the $\text{Al}-\text{O}$, $\text{Al}-\text{O}-\text{Si}$ vibrations and $\text{Si}-\text{O}$ bending vibrations, respectively (Valášková et al., 2020; Brião et al., 2021). Similar IR adsorption bands can be found in Fig. 4(b), indicating that the crystal structure of Vt is independent with the reducing-charge and organic treatment.

Compared with the Vt and Vt-2, all FT-IR spectra of *bis*-N-heterocyclic-based organo-Vts display additional weak bands at around 2929 and 2854 cm^{-1} , which are attributed to the characteristic stretching vibrations of $-\text{CH}_3$ and $-\text{CH}_2$ of the *bis*-N-heterocyclic salts (Zhou et al., 2020; Ge et al., 2021), and the small bands at around 1468 cm^{-1} are ascribed to the bending vibrations of the $\text{C}-\text{H}$ in the *bis*-N-heterocyclic quaternary ammonium salts (Caglar et al., 2016; Cheng et al., 2020). All these facts are a good

indication of the intercalation of the *bis*-N-heterocyclic salts into the layers of both the natural and reduced-charge vermiculites (Yu et al., 2010; Caglar et al., 2016).

3.4. TG-DTG analyses of vermiculites/organo-vermiculites

Given that their similar structures, the Vt and Vt-2 as well as their organic derivatives are chosen as the representatives for the TG-DTG analyses. The TG-DTG curves of the Vt, Vt-2 and organo-vermiculites show the similar but different mass losses processes with the temperature increasing (Fig. 5). As seen from Fig. 5(a) and (c), there are two distinct endothermic peaks of Vt at 87 and $195\text{ }^\circ\text{C}$, which are identified as the losses of the adsorbed and bound water of the Vt (4.63%), respectively (Caglar et al., 2016; Guo et al., 2019). Vt-2 exhibits the similar weight loss process (Fig. 5(b) and (d)), of which the mass losses (3.97%) appear at around 67 and $169\text{ }^\circ\text{C}$. The differences of weight losses between the Vt and Vt-2 may be caused by the treatment of layer charge reduction (Valášková et al., 2020). On the one hand, the heating treatment may release part of the water that retained in the vermiculite structure (Marwa et al., 2009); on the other hand, as the layer charge reduces, the hydrated interlayer cations decrease accordingly, lessening the water absorbed/bound in Vt (Ghaleh et al., 2020; Nowrouzi et al., 2020). For the organo-Vts modified by *bis*-N-heterocyclic salts, the weight losses occur at the range of 50 – $200\text{ }^\circ\text{C}$ are attributed to the release of the adsorbed water. The additional decreases in mass of *bis*-N-heterocyclic-based organo-Vts at around $400\text{ }^\circ\text{C}$ are belonging to the decomposition of *bis*-N-heterocyclic quaternary ammonium salts (Wu et al., 2015; Caglar et al., 2016), suggesting the successful intercalation of these *bis*-N-heterocyclic salts into the vermiculites, which can be corroborated with the results of FT-IR.

Interestingly, compared with the weight losses of the decomposition of *bis*-N-heterocyclic quaternary ammonium salts adsorbed on the Vt (1.82%–3.26%), that of organic reduced-charge

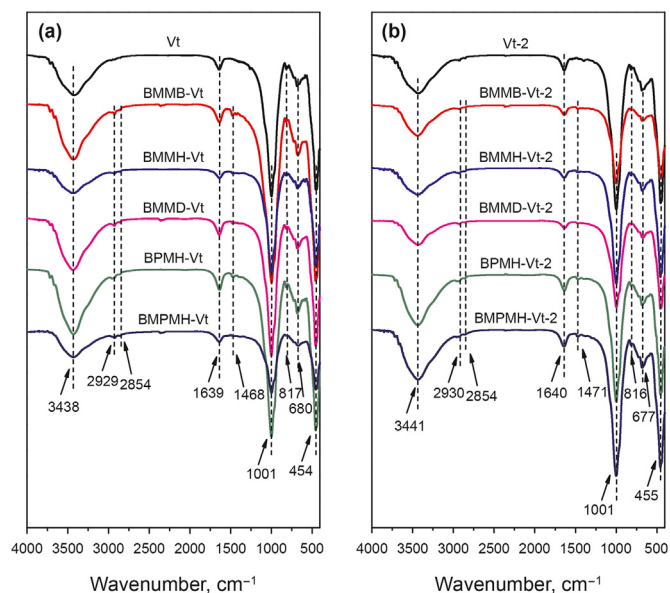


Fig. 4. The FT-IR spectra of the Vts and *bis*-N-heterocyclic-based organo-Vts.

vermiculite are lower to 1.65%–2.97%. It can be calculated that the loading amounts of BMMB, BMMH, BMMD, BPMH and BMPMH cations (without Br⁻) are 0.130/0.119, 0.094/0.075, 0.058/0.049, 0.092/0.072 and 0.059/0.056 mmol on 1.0 g Vt/Vt-2, respectively. The loading amounts of *bis*-N-heterocyclic cations decrease with the layer charge of the Vts decreasing. This is caused by the fact that the layer charge of the clay serves as the main binding site for the adsorption/intercalation of the *bis*-N-heterocyclic salts (Luo et al., 2014b). Meanwhile, the structure of the *bis*-N-heterocyclic cations also shows a negative influence on the amounts of organic cations inserted into the particle, resulting by the steric hindrance between the organic cations. In addition, after modification, all of the losses of organo-Vts within 200 °C are around 1.87%–2.93% that lower than that of Vt and Vt-2, indicating that the inserted *bis*-N-heterocyclic cations cover the vermiculite, resulting in a more hydrophobic surface (Wu et al., 2015).

3.5. BET analyses of vermiculites/organo-vermiculites

The BET specific surface areas of vermiculites and *bis*-N-heterocyclic-based organo-vermiculites are listed in Table 2. Seen from the Table 2, the surface area of Vt is 11.77 m² g⁻¹ that is lower than that of Vt-2 (17.14 m² g⁻¹). It can be ascribed as the migration of

cations into the silicate layer and the dehydration of vermiculite during the reduction of layer charge (Malla and Douglas, 1987; Marwa et al., 2009), providing the chance for more N₂ probe molecules to enter the interlayer space. However, the organo-vermiculites inserted by *bis*-N-heterocyclic salts show the relatively lower surface areas than the original ones. It may be attributed to the formation of monolayer of *bis*-N-heterocyclic quaternary ammonium salts in the layers, therefore, resulting in the steric hindrance of N₂ probe (Caglar et al., 2016). Knowing that the exchanging of organic cations in clay mineral change the surface area, which depends on their structure and arrangement. As the *bis*-morpholinyl cations inserted into the vermiculites, the surface areas of the organo-clays are as follow: BMMH-Vt > BMMB-Vt > BMMD-Vt, which suffers by the spacer length of organic cation and the enlarged interlayer spaces of vermiculite (Luo et al., 2014a). After cationic exchange, the interlayer space is filled by organic cations, and the specific surface area of the particle reduces with the spacer length increasing, resulting in the steric hindrance of the N₂ probe. But for BMMH-Vt, it may be related to the cavity in the enlarged interlamination that formed by the inserted BMMH cations, which allows the N₂ molecules to access the interlayer surface, and the resembling phenomenon also has been reported by Luo et al. (2014a). Similar trend also can be found in the alteration of surface areas of organo-Vt-2. Compared with the *bis*-N-heterocyclic cations with same spacer but different headgroups (*i.e.* morpholinium, piperidinium and piperazinium), it can be found that the sequence of the surface areas of *bis*-N-heterocyclic-containing organo-Vts is BMMH-Vt > BPMH-Vt > BMPMH-Vt. This fact may be due to the steric hindrance caused by the BMPMH with larger headgroup (4-methylpiperazinium), preventing the N₂ probe from entering the interlamination of Vt. But for Vt-2, the surface area modified by BMPMH is slightly larger than that of BPMH, which may be caused by the relatively loose arrangement in the reduced-charge vermiculites. Moreover, due to the electrostatic interaction between the surface and organic cations (Wu et al., 2015), the packing density of the *bis*-N-heterocyclic cations decrease as the layer charge decreases, therefore, all of the organo-Vt-2 show the larger surface areas than that of organo-Vt.

3.6. SEM analyses of vermiculites/organo-vermiculites

The images of morphology of the natural and treated vermiculites are shown in Fig. 6. Seen from the Fig. 6(a) and (e), the raw Vt exhibits a typical lamellar structure, while the Vt-2 shows the fragmentized texture. As modified by the *bis*-N-heterocyclic quaternary ammonium salts, both the raw and reduced-charge vermiculites display the more broken and curved but layered structured lamella appearances (Fig. 6(b)–(d) and (f)–(h)), which is

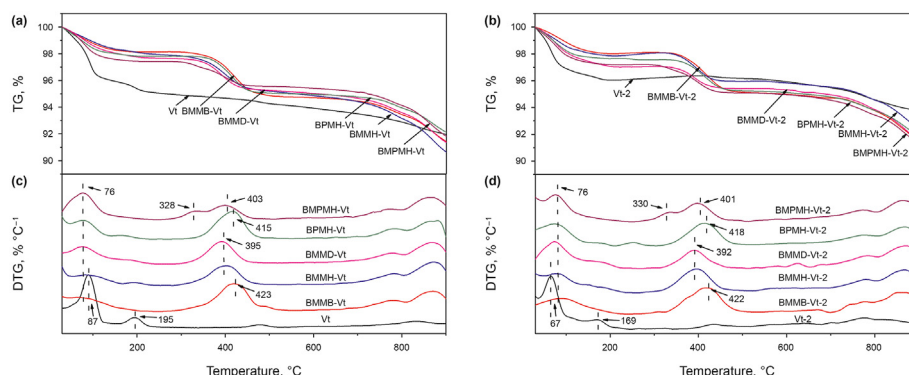


Fig. 5. The curves of TG and DTG of the Vts and *bis*-N-heterocyclic-based organo-Vts.

Table 2
BET surface areas of Vt, Vt-2, organo-Vts and organo-Vts-2.

	BET surface areas, m ² g ⁻¹		
Vt	11.77	Vt-2	17.14
BMMB-Vt	9.93	BMMB-Vt-2	14.78
BMMH-Vt	10.78	BMMH-Vt-2	15.14
BMMD-Vt	9.73	BMMD-Vt-2	13.54
BPMH-Vt	10.48	BPMH-Vt-2	14.10
BMPMH-Vt	9.20	BMPMH-Vt-2	14.21

caused by the interposition of the *bis*-N-heterocyclic cations into the layers of clay mineral.

3.7. Wettability alteration of organo-vermiculites

The wetting properties of the *bis*-N-heterocyclic-based organo-Vts are evaluated by capillary rise tests cooperated with *LHR* values. All of the wetting curves of organo-Vts modified by *bis*-N-heterocyclic salts towards oil and water phases are well fitted by linear least-square with the regression coefficients (R^2) of more than 0.99. The values of wetting rates (k_o and k_w for oil and water phases, respectively) of these *bis*-N-heterocyclic-based organo-Vts as well as the calculated *LHR* are tabulated in Table 3. As the *LHR* reflects the relative wettability conceptually, the greater the value, the more hydrophobicity of organoclays (Chang et al., 2009). Depicted in Table 3, the raw Vt shows the hydrophilic surface, while the reduced-charge vermiculites are relatively hydrophobic. After modification, all of organo-vermiculites show a lipophilic surface, in which the layer charge, spacer length and the N-heterocycle headgroups of modifiers play the role in the affinity for water and oil of organo-Vts.

3.7.1. Effect of layer charge

In terms of the change in layer charge, almost the values of k_w and k_o decrease firstly and then increase, that showing a waved change with the decreasing layer charge. As seen from Table 3, the values of k_w alter slightly but those of k_o are suffered the greater impact by charge alteration, and the calculated *LHR* values of organo-vermiculites decreases as follows: organo-Vt > organo-Vt-1 > organo-Vt-2 > organo-Vt-3, which is consistent with the decreasing trend of layer charge. Based on the electrostatic interaction between negatively charged surface and positively charged organics (Wu et al., 2015), the binding site on the surface are lessened as the charge reduces, resulting in the decline in the intercalated *bis*-N-heterocyclic cations, which is confirmed by the results of TG, and the broadening in the distance between the cations accordingly (Bujdák et al., 2007). Thereby, the tightly organic monolayer of *bis*-N-heterocyclic quaternary ammonium

salts that formed in vermiculite layers turns to be loosened as the layer charge decreases, leading to the reduction of the affinity towards the oil phase and more hydrophilic surface of *bis*-N-heterocyclic-based organo-Vts. In summary, the layer charge controls the loading and arrangement of intercalated *bis*-N-heterocyclic salts, of which the reduction may provide the possibility for the alteration in hydrophilicity of organo-clays.

3.7.2. Effect of spacer length of bis-morpholinium salts

Not only the layer charge affects the wettability of organo-vermiculites, but also the structure of the modifiers bears on the alteration (Wang et al., 2019; Ding and Gao, 2021). Independent of the change in layer charge, the relatively wettability of morpholinium-containing organo-Vts that represented by *LHR* value is as the following order: BMMD-Vts > BMMH-Vts > BMMB-Vts, which may be related to both of the hydrophobicity of the modifier and their arrangement in layers. On the one hand, as the spacer length increases, the lipophilicity of the modifier increases correspondingly, which may lead to the organic phases in layers more hydrophobicity after modification. On the other hand, combined with the results of characterizations, the inserted BMMD cations that own long spacer may form the relatively compact organic monolayer with a lying flat configuration in the interlayer space of Vts, which lowers the specific surface area of organo-Vts, and thereby, resulting in the more hydrophobic surface. That is to say, the longer the spacer length of *bis*-morpholinium modifier, the more hydrophobic of the morpholinium-based organo-Vts.

3.7.3. Effect of N-heterocyclic headgroups

In spite of the spacer length, the type of modifier that owns different N-heterocyclic headgroup also affects the wetting properties of organo-Vts. As displayed in Table 3, the sequence of the wettability of organo-vermiculites altered by different N-heterocyclic cations is as follows: BMPMH-Vts > BPMH-Vts > BMMH-Vts. Owing to the similar structure of BMPMH, BPMH and BMMH (shown in Fig. 1), the component in N-heterocyclic headgroups may result in the difference in the wetting behaviors of the *bis*-N-heterocyclic-based organo-Vts. After intercalated into the vermiculites,

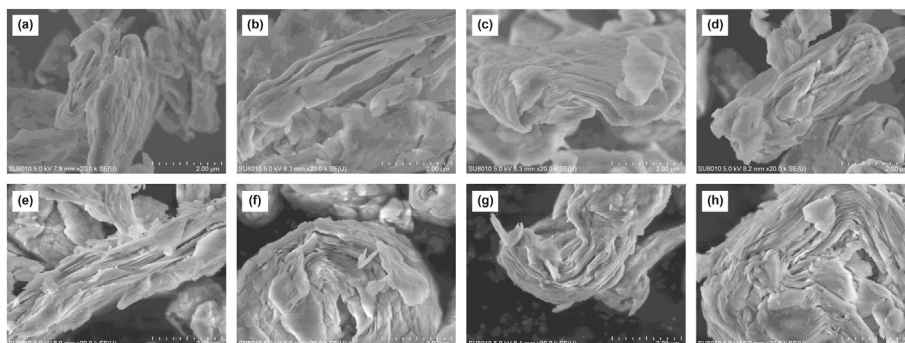


Fig. 6. The SEM images of Vt (a), Vt-2 (e), organo-Vt and organo-Vt-2 modified by BMMH (b, f), BPMH (c, g) and BMPMH (d, h), respectively.

Table 3
The values of k_o , k_w and LHR of organo-Vts.

	Vt			Vt-1			Vt-2			Vt-3		
	k_o , $\text{kPa}^2 \text{s}^{-1}$	k_w , $\text{kPa}^2 \text{s}^{-1}$	LHR	k_o , $\text{kPa}^2 \text{s}^{-1}$	k_w , $\text{kPa}^2 \text{s}^{-1}$	LHR	k_o , $\text{kPa}^2 \text{s}^{-1}$	k_w , $\text{kPa}^2 \text{s}^{-1}$	LHR	k_o , $\text{kPa}^2 \text{s}^{-1}$	k_w , $\text{kPa}^2 \text{s}^{-1}$	LHR
-	0.066	0.142	1.29	0.032	0.028	3.17	0.030	0.026	3.20	0.043	0.037	3.22
BMMB	0.261	0.150	4.82	0.139	0.094	4.10	0.109	0.076	3.98	0.116	0.097	3.31
BMMH	0.391	0.209	5.19	0.191	0.115	4.60	0.112	0.069	4.50	0.109	0.088	3.43
BMDM	0.207	0.096	5.98	0.126	0.064	5.46	0.129	0.071	5.04	0.098	0.072	3.77
BPMH	0.195	0.094	5.75	0.191	0.112	4.73	0.171	0.102	4.65	0.143	0.110	3.60
BMPMH	0.218	0.104	5.81	0.116	0.060	5.36	0.162	0.090	4.99	0.097	0.073	3.68

the additional CH_3 groups in the piperazinium headgroups of BMPMH may cause the hindrance of water to enter the interlayer space, leading to the more water-repelled surface (Kawamura et al., 2017). While for BMMH with the morpholinium headgroups that contain the oxygen atoms, the weakly hydrogen bond may be formed between the BMMH and water (Dai et al., 2017), therefore, resulting in a relatively hydrophilic surface of *bis*-N-heterocyclic-based organo-Vts. Compared with BMPMH and BMMH, BPMH owns the smaller headgroups than BMPMH, but more hydrophobic than BMMH, which gives rise to the moderate hydrophobic of BPMH-Vts among these *bis*-N-heterocyclic-based organo-Vts. In general, BMPMH may lead to Vt more hydrophobic due to the larger structure size and steric effect of the piperazinium headgroup with $\text{N}-\text{CH}_3$ in BMPMH than the CH_2 and O in the piperidinium (BPMH) and morpholinium (BMMH). And the O atoms in *bis*-morpholinium salts may form the weak hydrogen bond with water, which endows the most hydrophilic surface of *bis*-N-heterocyclic-based organo-Vts.

In conclusion, layer charge of Vt, spacer length and the type of the N-heterocyclic headgroup of modifier have the synergistic effect on the regulation of the wettability. The more the layer charge of Vt, the longer the spacer length and the larger/more nonpolar the headgroup of *bis*-N-heterocyclic quaternary ammonium salts, the more hydrophobic the *bis*-N-heterocyclic-based organo-Vts.

4. Conclusion

In this work, vermiculite and its derivatives with reduced-charge treated by Li^+ -saturated heating method, and series of *bis*-N-heterocyclic quaternary ammonium salts with different spacer length and N-heterocyclic groups have been synthesized and employed for altering the wettability of the high-charged clay mineral. Several characterization methods are used for monitoring the structure of the raw and organo-vermiculites. The results of XRD, FT-IR and TG-DTG indicate that all of the *bis*-N-heterocyclic salts have been successfully inserted into the Vts layers, forming the organic monolayer. The morphology of Vts and *bis*-N-heterocyclic-based organo-Vts are collected by SEM, suggesting that all of the samples still keep the stratified structure, while the BET surface areas of Vts changes after modification, which may be related to the arrangement of intercalated *bis*-N-heterocyclic cations that cover and/or provide the cavity of surface. The results of capillary rise tests combined with LHR values unveil the wettability alteration of the organo-Vts tuned by *bis*-N-heterocyclic salts. With the layer charge decreasing, the hydrophilicity of the *bis*-N-heterocyclic-based organo-Vts gradually increases, which is probably caused by the decline in binding sites. As the result of the change in spacer length of modifier, the wetting properties of organo-Vts modified by *bis*-morpholinium salts changes in order of BMDM-Vts > BMMH-Vts > BMMB-Vts, and difference in N-heterocyclic groups of modifiers leads to the sequence of wettability: BMPMH-Vts > BPMH-Vts > BMMH-Vts. Both of the layer charge of vermiculites and the spacer and N-heterocyclic groups of modifiers have the synergetic

effect on wettability alteration. The more the layer charge of Vt, the longer the spacer length and the larger/more nonpolar the headgroup of *bis*-N-heterocyclic modifier, the more hydrophobic the *bis*-N-heterocyclic-based organo-Vts. These results can help for the further understanding of the effect of structure of different type of modifiers on the wettability alteration of different charged mineral, and give the new thought and theoretical recommendations for designing the wetting modifier of clay mineral.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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