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# Influence of different exchangeable cations ( $\text{Li}^+$ , $\text{Na}^+$ , $\text{Ca}^{2+}$ ) on the modification effects and properties of organomontmorillonites used in oil-based drilling fluids/muds

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Montmorillonite with different exchangeable cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ) in the inter spaces were modified by cationic and anionic surfactants together, to prepare cationic-anionic organomontmorillonites (Li-organomontmorillonite, Na-organomontmorillonite and Ca-organomontmorillonite). Prepared organomontmorillonites were used in oil-based drilling fluids. Structure and properties of the cationic-anionic organomontmorillonites were studied by X-ray diffraction, thermogravimetry and contact angles. Properties of different oil-water ratios oil-based drilling fluids/muds adding organomontmorillonites at room and high temperatures were studied by rotary viscometer, filtration loss apparatus and six-speed viscosimeter. The results showed exchangeable cations in the inter spaces of montmorillonite had an obvious impact on the structure and properties of the cationic-anionic organomontmorillonites. Of three kinds of cationic-anionic organomontmorillonites, cationic-anionic organomontmorillonites prepared from Li-montmorillonite had the largest basal spacing, best thermal stability and highest surface polarity which followed by Na-montmorillonites and Ca-montmorillonite successively. Applied research of oil-based drilling fluids/muds adding different organomontmorillonites showed that Li-organomontmorillonite showed best applied properties in full oil-based drilling fluids/muds at 180°C. Na-organomontmorillonite showed best applied properties in 80:20 / 90:10 oil-water ratio oil-based drilling fluids/muds at 180°C. The oil-based drilling fluids/muds adding Ca-organomontmorillonite had worst application at 180°C.

## 1. Introduction

Montmorillonite (Mt) is layered silicate mineral which composes of two corner-connected silica-oxygen tetrahedral sheets sandwiching a common edge aluminum octahedral sheet. Because of replacement of aluminum ions in the octahedral sheet by low valence metal cations, layers of Mt are permanently electronegativity. Metal cations such as sodium and calcium are attracted to the mineral laminate to neutralize the negative layer charges<sup>1</sup>, thus form Na-Mt and Ca-Mt.

Mt with different exchangeable cations in the interlayer spaces were studied by shape, size<sup>2</sup>, dye adsorption<sup>3</sup>, physical and electrical properties<sup>4, 5</sup>, which revealed exchangeable cations in the interlayer of Mt had an impact on the resulting properties of Mt. Also, the cations in the interlayer of Mt can be exchanged by organic molecules to prepare organomontmorillonites (OMt). Researches have studied the effects of exchangeable cations on the properties of

corresponding cationic OMt<sup>6</sup>, while the influences of exchangeable cations on the properties of cationic-anionic OMt (CA-OMt) are rarely reported.

Oil-based drilling fluids/muds (OBM), due to their excellent lubricity, high rate of penetration and outstanding thermal stability, are often used to drill difficult wells, such as high temperature and high pressure (HTHP) wells<sup>7</sup> and shale gas drilling. OMt as additives that can enhance and maintain the rheology of oil-based drilling fluids have drawn a lot of attention and research, and in most of it, Mt was modified by cationic surfactants<sup>9-12</sup> and by nonionic surfactants<sup>13, 14</sup>.

In previous study, existing OBM adding cationic-OMt or non-ionic-OMt often fails below 140°C<sup>11, 12</sup>, thus cannot be applied in deep well. Compared with cationic-OMt or non-ionic-OMt, CA-OMt with better thermal stability<sup>15, 18</sup> have the advantage and potential to be widely applied in drilling wells under different conditions. Moreover, the existing OMt for use in OBM were prepared most from Na-Mt<sup>13, 14, 16</sup> and Li-Mt<sup>17</sup>, while research on comparison of the



OMt prepared by different kinds of Mt, and the effect of cation on the properties of OMt are still lacking.

In this study, CA-OMt were prepared from Mt with different exchangeable cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ) in the inter spaces by cationic and anionic surfactants together. The structure and properties of CA-OMt were studied by X-ray diffraction, thermogravimetry and contact angles. The performances of different oil-water ratios OBM adding CA-OMt at different temperatures (25°C, 150°C and 180°C) were further compared by rotary viscosimeter, filtration loss apparatus and six-speed viscosimeter, effects of cation on the properties of CA-OMt were revealed .

## 2. Materials and Methods

### 2.1 Materials

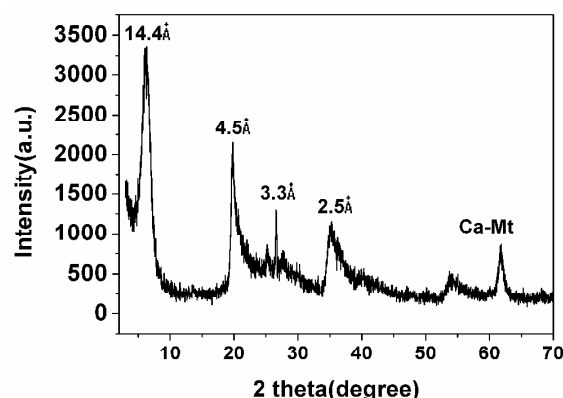
Ca-Montmorillonite (Ca-Mt) is purchased from Ning cheng, Inner Mongolia, China, with the purity of 96%. The Ca-Mt was ground and passed through a 200-mesh sieve, dried under 60°C without further purification. The cation exchangeable capacity (CEC) of Ca-Mt was 78mmol/100g. XRD pattern of Ca-Mt was shown in Fig.1. The results of chemical composition are shown in Tab.1.

Na-Mt is prepared from Ca-Mt by  $\text{Na}_2\text{CO}_3$  according to Wu et al.<sup>18</sup>. First, 10 g Ca-Mt was added into 100 ml distilled water and stirred at 1000 r/min for 30 minutes, then 0.4 g  $\text{Na}_2\text{CO}_3$  (calculated from CEC) was added into the suspension and the system was stirred for another 60 minutes. At the end, the resulting suspension was separated by centrifugation and dried at 60°C for 24 h. Sample was ground and passed through a 200-mesh sieve to obtained Na-Mt. Li-Mt is prepared from Ca-Mt by  $\text{Li}_2\text{CO}_3$  in the same way.

The liquid organic dispersion media is commercial 0# diesel oil with density of 0.853 g/cm<sup>3</sup> at 25°C. The cationic surfactant Cetyltrimethyl Ammonium Bromide (CTAB) and  $\text{CaCl}_2$  were analytical reagent, purchased from Beijing chemical works, China. Anionic surfactant Sodium Dodecyl Sulfate (SDS) was chemically pure and purchased from Shantou Xilong Co., Ltd., China. Barite was technical grade, which was also purchased from Shantou Xilong Co., Ltd.,

**Tab.1** Chemical composition of Ca-Mt (loss on ignition 1.6%)

Composition	$\text{CO}_2$	$\text{Na}_2\text{O}$	$\text{MgO}$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{CaO}$	$\text{TiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{P}_2\text{O}_5$
Wt %	16.5	0.2	4.0	14.7	48.0	3.4	1.8	8.9	0.9



**Fig.1** XRD pattern of Ca-Mt

### 2.2 Preparation of OMt and OBM

#### 2.2.1 Preparation of cationic organomontmorillonites

Cationic organomontmorillonites (cationic-OMt) were prepared from different Mt through mechanochemistry<sup>19</sup> with CTAB equivalent to 1.5 CEC. 10 g Mt, CTAB equivalent to 1.5 CEC of Mt were mixed and milled by a planetary ball mill at 500 r/min for 1 hour. Samples were dried at 60 °C for 24 h and finally milled to pass through a 200-mesh sieve. Mt with  $\text{Ca}^{2+}$  as exchangeable cations modified by CTAB was named as Ca-CTAB, other OMt were denoted in the same way as Li-CTAB and Na-CTAB.

#### 2.2.2 Preparation of CA-OMt

Different CA-OMt were prepared from Mt by CTAB equivalent to 1.5 CEC and SDS equivalent to 0.6 CEC in the process of mechanochemistry<sup>19</sup> as mentioned in 2.2.1. Mt with  $\text{Ca}^{2+}$  as exchangeable cations modified by CTAB and SDS was named as Ca-CTAB+SDS, other CA-OMt were denoted in the same way as Li-CTAB+SDS and Na-CTAB+SDS.

#### 2.2.3 Preparation of OBM with different oil-water ratios

The OBM with different oil-water ratios were prepared according to field study in BHDC: 300 ml/270 ml/240 ml (according to different oil-water ratios) 0# diesel, 10 g BZ-OPE and 10 g BZ-OSE (emulsifiers) were placed in a blender and blended for 5 min at the speed of 10000 r/min to produce the base-fluid (an emulsion). Then, 12.5 g  $\text{Ca}(\text{OH})_2$  and 6 g CA-OMt were added to the base-fluid emulsion and the mixtures were blended for 20 min at the speed of 10000 r/min. At last, 0 ml/30 ml/60 ml (according to different oil-water ratios) 20% concentration  $\text{CaCl}_2$  solution and 806 g barite were added into the emulsion then the emulsion was



blended for another 30 min at 10000 r/min. The resulting OBM were tested first and placed in a rotary oven heated to 150°C and 180°C, where they were aged for 16 h and tested again.

## 2.3 Characterization methods

### 2.3.1 XRD

X-ray powder diffraction (XRD) analysis was performed on a D/max-rA 12 kW diffraction at 40 kV and 100 mA using a Cu tube (Cu Ka target,  $\lambda = 0.154$  nm) at a scanning rate of 4 °/min.

### 2.3.2 Thermal stability

The Thermal Gravity (TG), Differential thermal gravity (DTG) and Differential Thermal Analysis (DTA) analysis were conducted on Shimadzu DTA-TG simultaneously measuring device DTG-60 under air atmosphere. A heating rate of 10°C /min was applied until the temperature reached 900 °C.

### 2.3.3 Contact angle

Contact angle was measured by ALB-XY-50-3JL from Zhong chen Instrument Co., Ltd, Shanghai. The sessile drop method was used for the surface polarity measurement of the CA-OMt. A video camera equipped with a homemade image analysis device allowed the measurement of contact angle between deionized water and the surface of CA-OMt.

### 2.3.4 Properties of OBM

The apparent viscosity(AV), plastic viscosity (PV), yield point (YP), filtration, yield point and plastic viscosity ratio (YP/PV) and shear thinning index of OBM were measured according to API Recommended practice of Standard procedure for field testing drilling fluids<sup>20</sup>:

$$\text{Apparent viscosity: } \mu_a = \Phi_{600}/2 \text{ (cP),}$$

$$\text{Plastic viscosity: } \mu_p = \Phi_{600} - \Phi_{300} \text{ (cP),}$$

Yield point:  $y_p = \Phi_{300} - \mu_p \cdot 0.5 \text{ N/m}^2 \text{ (lb/100ft}^2\text{)}$ , Yield point and plastic viscosity ratio:

Yield point/Plastic viscosity, Shear thinning index: gel strength (10 min)/gel strength (10 s),

ZNN-D6S six-speed viscometer and an API filtration testing instrument from Haitongda, Qingdao Co., Ltd., China were used.

### 2.3.5 Thixotropy

Thixotropy of OBM adding different OMT was tested according to GB27798-2011, by ThermoHAAKE RV1 rotary

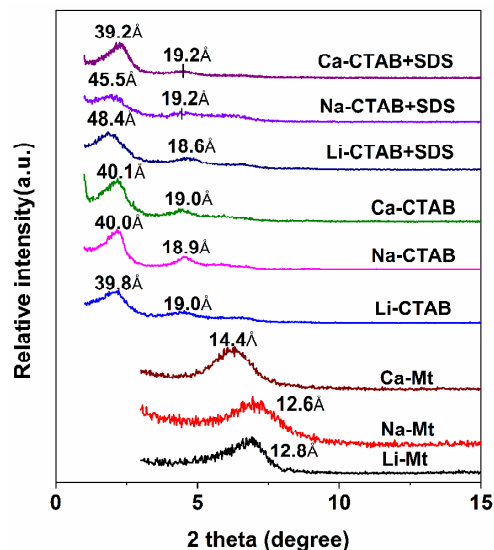


Fig.2 XRD patterns of Mt and OMT

viscosimeter from Thermo Electron (Karlsruhe) GmbH, Germany. The surface area of a hysteresis loop can be used as a measure for the degree of thixotropy.

## 3. Results and discussion

### 3.1 Preparation and properties of OMT

#### 3.1.1 XRD of Mt and OMT

XRD patterns of Li-Mt, Na-Mt, Ca-Mt and OMT were shown in Fig.2.

Diffractions of different Mt and OMT were shown in Fig.2. The  $d_{001}$  values of Li-CTAB, Na-CTAB and Ca-CTAB were 39.8 Å, 40.0 Å and 40.1 Å, respectively. The  $d_{001}$  values of Li-CTAB+SDS, Na-CTAB+SDS and Ca-CTAB+SDS were 48.4 Å, 45.5 Å and 39.2 Å, respectively. Comparing XRD pattern of Ca-CTAB with that of Ca-CTAB+SDS, there was no significant change in  $d_{001}$  value or diffraction regularity, and basal spacing of Ca-Mt modified with CTAB and SDS by mechanochemistry was also obviously smaller than that of Ca-Mt modified with CTAB and SDS through solution intercalation method according to Wu et al.<sup>18</sup> and Zhang et al.<sup>15</sup>. Both of the results indicated that SDS hardly intercalated into the interlayer of Ca-CTAB. During the modification process, CTAB molecules were first intercalated into the interlayer of Mt by ion exchange and mechanochemistry, so modification effect of Li-CTAB, Na-CTAB and Ca-CTAB were almost same. Then CTAB and SDS molecules



intercalated into the interlayer of cationic-OMt by mechanichemistry. With stronger exfoliated structure of cationic-OMt, more amount of SDS can intercalate into it. Moreover, residual exchangeable cations that did not exchanged by CTAB had an effect on the exfoliated structure of cationic-OMt. The greater valence of cations remained in the inter spaces of cationic-OMt, the worse exfoliated structure of cationic-OMt achieved, so less amount of SDS intercalated into it. Compared with weaker bond energy between  $\text{Li}^+/\text{Na}^+$  with Mt laminate, stronger bond energy between  $\text{Ca}^{2+}$  and Mt laminate resulted in less activity and exfoliated structure of Ca-Mt. Under the same mechanical force, SDS molecules can hardly intercalate into the interlayer of Ca-CTAB. However, XRD patterns of Li-CTAB+SDS and Na-CTAB+SDS showed significantly larger basal spacing compared with  $d_{001}$  values of corresponding Li-CTAB and Na-CTAB (shown in Fig. 2), indicating both of CTAB and SDS had efficiently intercalated into the inter spaces of Li-Mt and Na-Mt. For both Li-Mt and Na-Mt, weaker bond energy between cations and Mt laminate resulted in more activity and stronger exfoliated structure of cationic OMt in the process of modification, which leading to more amount of SDS intercalated into the interlayer and better modification effect of corresponding CA-OMt. Results above showed the type of exchangeable cations in the inter spaces of Mt hardly had an impact on the modification effect of basal spacing of cationic-OMt, while had an obvious influence on the basal spacing of CA-OMt. With higher  $d_{001}$  value, more amount of surfactants were intercalated into the interlayer of Mt. The greater valence of cations in the inter spaces of Mt, the worse modification effect of resulting CA-OMt prepared. Li-Mt and Na-Mt were successfully modified by cationic and anionic surfactants together, while the modification status of Ca-CTAB+SDS was not sure. With the best activity of cations in the inter spaces of Mt, Li-Mt and Na-Mt were modified sufficiently through mechanochemistry and more amount of organic matter were intercalated into the interlayer of Li-CTAB+SDS and Na-CTAB+SDS than Ca-CTAB+SDS.

### 3.1.2 Thermal stability of OMt

TG, DTG and DTA were used to investigate the thermal stability of Li-CTAB+SDS, Na-CTAB+SDS and Ca-CTAB+SDS, the results were illustrated in Fig. 3.

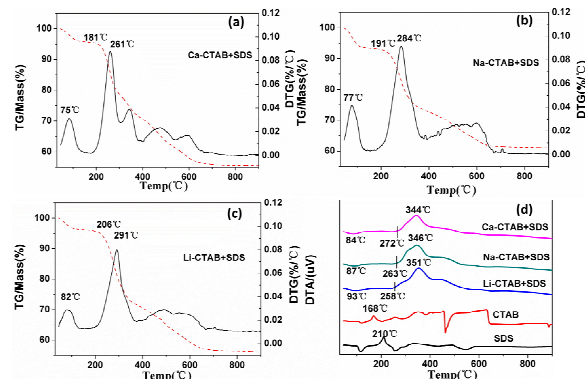


Fig. 3 TG, DTG and DTA curves of OMt

Prepared from Ca-Mt, Na-Mt and Li-Mt modified by same amount of surfactants, Ca-CTAB+SDS, Na-CTAB+SDS and Li-CTAB+SDS showed significant endothermic peak and obvious exothermic peak in Fig. 3 (d). The first endothermic peaks appeared at 84°C, 87°C and 93°C for Ca-CTAB+SDS, Na-CTAB+SDS and Li-CTAB+SDS respectively. They could be related to the loss of water molecules exterior to the layers of CA-OMt<sup>1, 21</sup>, and the lower endothermic peak temperature indicated the weaker adsorption between water molecules and the surface of CA-OMt. With the same amount of surfactants used during modification process, less amount of surfactants can intercalate into the inter spaces of Ca-CTAB+SDS (shown in 3.1.1), thus more amount of them were adsorbed on the surface of Ca-CTAB+SDS, which leading to the weaker adsorption and less residual of water molecules on the surface of Ca-CTAB+SDS among three CA-OMt. Small organic molecules on the surface of Ca-CTAB+SDS, Na-CTAB+SDS and Li-CTAB+SDS started to decompose at 181°C, 191°C and 206°C, respectively. Decomposition of CTAB and SDS occurred at higher temperatures. The exothermic peaks in Fig.3 (d) illustrated the decomposition of surfactants in CA-OMt. For surfactants in each CA-OMt, the surfactants on the surface decomposed first, and the surfactants in the inter spaces of CA-OMt decomposed later at higher temperatures. Amount of SDS on the surface of CA-OMt decreased in the sequence of Ca-CTAB+SDS, Na-CTAB+SDS and Li-CTAB+SDS, so the synergistic effect between CTAB and SDS on the outer surface of CA-OMt weakened. Weakening synergistic effect between surfactants led to the earlier decomposition of CTAB and SDS together on the outer surface of Li-CTAB+SDS and Na-CTAB+SDS than that in



Ca-CTAB-SDS. For Li-CTAB+SDS and Na-CTAB+SDS, surfactants exterior the surfaces started to decompose at 258°C and 263°C, lower than that in Ca-CTAB+SDS (272°C). While with more surfactants intercalated in the inter spaces of Li-CTAB+SDS and Na-CTAB+SDS, the decomposition of cationic and anionic surfactants in the inter spaces of Li-CTAB+SDS and Na-CTAB+SDS occurred at higher temperatures<sup>22</sup> and reached their peaks at 351°C and 346°C according to DTA curves in Fig. 3 (d). Decomposition of cationic and anionic surfactants in the inter spaces of Ca-CTAB+SDS occurred at 344°C. In Fig.3 (a), (b) and (c), loss rate of surfactants in Ca-CTAB+SDS, Na-CTAB+SDS, Li-CTAB+SDS reached their peaks at 261°C, 284°C and 291°C, respectively, indicating the thermal stability order of surfactants in the interlayer of CA-OMt was Li-CTAB+SDS, Na-CTAB+SDS, Ca-CTAB+SDS, which corresponded to the results in DTA. In accordance with the results in 3.1.1, the amount of SDS intercalated into the inter spaces of Li-CTAB+SDS and Na-CTAB+SDS are more than Ca-CTAB+SDS. So, the decomposing temperature of surfactants in Li-Mt and Na-Mt are higher than Ca-CTAB+SDS. The results above illustrated that cation in the interlayer of Mt had an effect on the amount of SDS intercalated into the inter spaces of CA-OMt and the thermal stability of CA-OMt. With the most active cation in the interlayer of Mt, Li-CTAB+SDS had the best modification effect, most amount of SDS in the inter spaces and the best thermal stability, which followed by Na-CTAB+SDS and Ca-CTAB+SDS.

### 3.1.3 Surface polarity of CA-OMt

The contact angles of Li-Mt, Na-Mt, Ca-Mt and different OMt were presented in Fig. 4.

After organic modification, contact angles of all CA-OMt

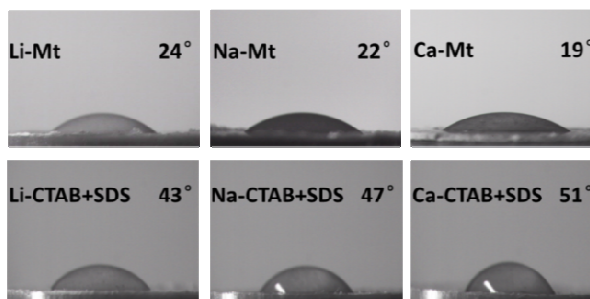


Fig. 4 Contact angles of Mt and different OMt

increased a lot compared with original Mt, indicating Mt had been organically modified efficiently. According to the discussions in 3.1.1, amount of surfactants on the surface of CA-OMt increased in the order of Li-CTAB+SDS, Na-CTAB+SDS and Ca-CTAB+SDS, thus leading to the fall of surface polarity and increasing of contact angles of them. Lower surface polarity and weaker adsorption between water and surface of CA-OMt led to the earlier loss of free water in CA-OMt, which corresponded to the results in 3.1.2 that water molecules in Ca-CTAB+SDS lost earlier than that in Na-CTAB+SDS and Li-CTAB+SDS. Results in 3.1.3 showed Ca-CTAB+SDS had the lower surface polarity among three CA-OMt, while Li-CTAB+SDS and Na-CTAB+SDS had higher surface polarity. To better enhanced the rheology and application of OBM, OMt had to disperse well in OBM and had high affinity to OBM. So OMt with appropriate contact angles and organic matters in the interlayer can disperse best in corresponding OBM.

## 3.2 Properties of OBM added by OMt

### 3.2.1 Thixotropy of 90:10 oil-water ratio OBM adding OMt

Thixotropy of 90:10 oil-water ratio OBM added by Li-CTAB+SDS, Na-CTAB+SDS, Ca-CTAB+SDS separately at 25°C, 150°C and 180°C were shown in Fig.5.

Thixotropy of 90:10 oil-water ratio OBM was tested at 25°C, 150°C and 180°C to evaluate the thermal stability and thixotropy of OBM added by Li-CTAB+SDS, Na-CTAB+SDS and Ca-CTAB+SDS, respectively. Results in Fig.5 revealed that the thixotropy of OBM added different OMt changed

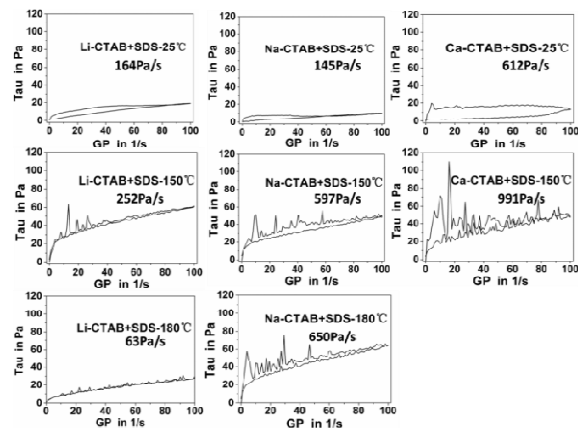


Fig. 5 Thixotropy of OBM adding OMt at different temperatures



significantly. At 25°C, hysteresis loop areas of OBM with Ca-CTAB+SDS, Na-CTAB+SDS and Li-CTAB+SDS were 612 Pa/s, 145 Pa/s and 164 Pa/s, respectively. Among them, hysteresis loop area of OBM with Ca-CTAB+SDS was the largest, while hysteresis loop areas of Na-CTAB+SDS and Li-CTAB+SDS were close. At 150°C, hysteresis loop area of OBM with Ca-CTAB+SDS, Na-CTAB+SDS and Li-CTAB+SDS were 991 Pa/s, 597 Pa/s and 252 Pa/s, respectively. Hysteresis loop area of OBM with Ca-CTAB+SDS was also the largest. At 180°C, OBM with Li-CTAB+SDS and Na-CTAB+SDS were still stable, the hysteresis loop areas of corresponding OBM were 63 Pa/s and 650 Pa/s, respectively. However, due to a lot of surfactants covered on the surface and poor thermal stability of Ca-CTAB+SDS, OBM with Ca-CTAB+SDS became curing state and lost its function. The results showed that CA-OMt prepared from Mt with different exchangeable cations in the interlayer had an impact on the thixotropy and thermal stability of OBM, and the main reason was owing to the different amount of SDS intercalated into the inter spaces of Mt. According to the results in 3.1.1,  $d_{001}$  values of Ca-CTAB+SDS, Na-CTAB+SDS and Li-CTAB+SDS were 39.2 Å, 45.5 Å and 48.4 Å, respectively. The amount of SDS intercalated into the inter spaces of CA-OMt decreased in the following: Li-CTAB+SDS, Na-CTAB+SDS, Ca-CTAB+SDS, which leading to the exfoliation degree of CA-OMt in OBM decreased in the sequence of Li-CTAB+SDS, Na-CTAB+SDS and Ca-CTAB+SDS. The more exfoliation laminate of CA-OMt, the worse thixotropy it behaved. In 90:10 oil-water ratio OBM, Li-CTAB+SDS had the weakest interlayer force than other CA-OMt, resulting worst thixotropy in 90:10 oil-water ratio OBM. Ca-CTAB+SDS with the lowest  $d_{001}$  value had best thixotropy at low temperatures. Below 150°C, Ca-CTAB+SDS showed best thixotropy, while at 180°C, due to the decomposition of surfactants in the interlayer space and surfactants covered on the surface, thermal stability of Ca-CTAB+SDS dropped (also shown in 3.1.2). At last, OBM added by Ca-CTAB+SDS failed. In 90:10 oil-water ratio OBM, Ca-CTAB+SDS showed better thixotropy than other CA-OMt below 150°C. Above 150°C, thermal stability of Li-CTAB+SDS and Na-CTAB+SDS were better than Ca-CTAB+SDS, and Na-CTAB+SDS showed better

thixotropy in drilling fluids due to its moderate laminates structure. In the following part of experiment, shear thinning index was measured to illustrate the thixotropy of OBM added by different CA-OMt.

### 3.2.2 Influences of different CA-OMt on the applied properties of 80:20, 90:10 oil-water ratio and full oil OBM

80:20, 90:10 oil-water ratio and full oil OBM were prepared according to 2.2.3 by adding Li-CTAB+SDS, Na-CTAB+SDS and Ca-CTAB+SDS separately, the resulting OBM were called as Li-CTAB+SDS-OBM, Na-CTAB+SDS-OBM and Ca-CTAB+SDS-OBM. Properties of different OBM at 25°C, 150°C and 180°C were illustrated in Tab.2, Tab.3 and Tab.4. The OBM should possess appropriate viscosity, a finite yield point and high-shear thinning behavior for suspending and transferring drill cuttings to the surface<sup>23</sup>. The data in Tab.2, Tab.3 and Tab.4 showed viscosity, filtration losses, YP, YP/PV and shear thinning index of different oil-water ratios OBM at 25°C, 150°C and 180°C. Results showed CA-OMt with different  $d_{001}$  values had a significant influence on the applied properties of OBM. Below 150°C, all OBM adding Ca-CTAB+SDS showed better AV, YP and less filtration loss than OBM added by Li-CTAB+SDS or Na-CTAB+SDS.

**Tab.2** Properties of 80:20 oil-water ratio OBM adding different OMt

	Li-CTAB+SDS-OBM			Na-CTAB+SDS-OBM			Ca-CTAB+SDS-OBM		
	25	150	180	25	150	180	25	150	180
Temperatures(°C)	25	150	180	25	150	180	25	150	180
AV(mpa*s)	84	109	130	93	123	137	108	130	—
PV(mpa*s)	72	81	103	79	91	104	93	106	—
Filtration (ml)	18	19	21	17	18	19	17	16	—
YP(Pa)	12	27	27	14	32	32	15	24	—
YP/PV(Pa/mPs)	0.17	0.34	0.26	0.18	0.35	0.31	0.17	0.23	—
Shear thinning index	1.03	1.05	1.05	1.04	1.07	1.06	1.04	1.05	—

Note:—curing state

**Tab.3** Properties of 90:10 oil-water ratio OBM adding different

	OMt								
	Li-CTAB+SDS-OBM			Na-CTAB+SDS-OBM			Ca-CTAB+SDS-OBM		
Temperatures(°C)	25	150	180	25	150	180	25	150	180
AV(mpa*s)	78	102	122	85	115	126	100	127	—
PV(mpa*s)	62	72	103	66	78	89	85	97	—
Filtration (ml)	18	19	22	18	19	20	18	15	—
YP(Pa)	16	30	19	19	37	37	15	30	—
YP/PV(Pa/mPs)	0.26	0.42	0.19	0.30	0.47	0.42	0.18	0.31	—
Shear thinning index	1.08	1.09	1.03	1.08	1.10	1.05	1.11	1.13	—

**Tab.4** Properties of full oil OBM adding different OMt

	OMt								
	Li-CTAB+SDS-OBM			Na-CTAB+SDS-OBM			Ca-CTAB+SDS-OBM		
Temperatures(°C)	25	150	180	25	150	180	25	150	180
AV(mpa*s)	75	97	118	81	102	117	96	122	—
PV(mpa*s)	59	63	86	67	64	88	82	106	—
Filtration (ml)	19	19	19	18	19	20	19	16	—
YP(Pa)	16	34	32	14	38	29	14	16	—
YP/PV(Pa/mPs)	0.22	0.54	0.38	0.22	0.59	0.34	0.17	0.15	—
Shear thinning index	1.06	1.07	1.06	1.06	1.07	1.04	1.08	1.07	—

5 Shear thinning index of 90:10 oil-water ratio OBM adding Ca-CTAB+SDS was higher than other OBM adding Li-CTAB+SDS or Na-CTAB+SDS, which corresponded to the results in 3.2.1 that below 150°C, OBM adding Ca-CTAB+SDS had the best thixotropy. However, YP/PV of OBM adding Ca-CTAB+SDS was less significant than OBM adding Li-CTAB+SDS or Na-CTAB+SDS. All kinds of OBM adding Ca-CTAB+SDS became curing state and failed at 180°C. The results showed that thermal stability of all kinds of OBM adding Ca-CTAB+SDS are acceptable below 150°C. OBM adding Li-CTAB+SDS and Na-CTAB+SDS separately exhibited better viscosity, rheology and filtration losses at high temperature (180°C). With more amount of SDS in the interlayer of Li-CTAB+SDS and Na-CTAB+SDS, thermal stability of surfactants in the inter spaces of Li-CTAB+SDS and Na-CTAB+SDS improved (also shown in 3.1.2) thus enhanced and maintained the rheological and applied properties of corresponding OBM. However, with more

amount of surfactants on the surface, thermal stability of Ca-CTAB+SDS fell, thus weakened the properties of OBM adding Ca-CTAB+SDS at high temperatures. Attention should be paid that at the same condition, 80:20/90:10 oil-water ratio OBM adding Na-CTAB+SDS showed better rheology than that with Li-CTAB+SDS, which also corresponded to the thixotropy results in 3.2.1. With more amount of SDS inserted into the inter spaces and more polar interlayer environment of Li-CTAB+SDS, Li-CTAB+SDS would be excessively exfoliated in 80:20/90:10 oil-water ratio OBM, leading to worse viscosity in OBM. As a result, 80:20/90:10 oil-water ratio OBM adding Li-CTAB+SDS had worse rheological and applied properties compared with OBM adding Na-CTAB+SDS. Differed from OBM with water, laminate structure of Li-CTAB+SDS in full oil OBM can hardly be fully exfoliated, and AV and YP of full oil OBM adding Li-CTAB+SDS at 180°C were 118 mpa\*s and 32 Pa, which were slightly better than OBM adding Na-CTAB+SDS. Filtration losses of full oil OBM adding Li-CTAB+SDS and Na-CTAB+SDS were 19 and 20 ml, respectively. Full oil OBM adding Li-CTAB+SDS showed better viscosity, rheology and filtration losses. While in both 80:20 and 90:10 oil-water ratios OBM of high polarity, Na-CTAB+SDS illustrated better viscosity and gel properties than that of Li-CTAB+SDS.

Below 150°C, OBM adding Ca-CTAB+SDS showed better applied properties than that with Li-CTAB+SDS/Na-CTAB+SDS. At 180°C, OBM added with Ca-CTAB+SDS lost their function. From 25°C to 180°C, with most active cation in the interlayer of Li-Mt, Li-CTAB+SDS showed favorable thermal stability, viscosity, filtration resistance property and shear thinning behavior in full oil OBM, Na-CTAB+SDS illustrated better thermal stability, viscosity, filtration resistance property and shear thinning behavior in both 80:20/90:10 oil-water ratio OBM.

#### 4. Conclusion

Montmorillonites with different exchangeable cations (Li<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>) in the inter spaces were modified by cationic and anionic surfactants together. With greater valence metal cations in the interlayer of Mt,  $d_{001}$  values, thermal stability and surface polarity of CA-OMt decreased.  $D_{001}$  values of





cationic-anionic organomontmorillonites (Li-CTAB+SDS, Na-CTAB+SDS and Ca-CTAB+SDS) were 48.4 Å, 45.5 Å and 39.2 Å, respectively. Thermal stability and surface polarity of the CA-OMt had positive correlation with the basal spacing themselves.

The applied properties of OBM adding Li-CTAB+SDS, Na-CTAB+SDS and Ca-CTAB+SDS separately were further studied. With optimal laminate structure of CA-OMt, rheology of OBM can be significantly enhanced. The surface polarity, amount of organic matter in the interlayer and the laminate structure of CA-OMt affect the properties of CA-OMt and the application of OBM. Below 150°C, Ca-CTAB+SDS with moderate laminate structure showed best properties in different oil-water ratios OBM. At 180°C, OBM adding Ca-CTAB+SDS failed to curing state. Below 150°C, OBM adding Li-CTAB+SDS/Na-CTAB+SDS showed favorable properties. At 180°C, Li-CTAB+SDS and Na-CTAB+SDS with more amount of surfactants in the interlayer showed better thermal stability in all OBM than Ca-CTAB+SDS. In full oil OBM, Li-CTAB+SDS showed best applied properties than Na-CTAB+SDS. In 80:20/90:10 oil-water ratios OBM, Na-CTAB+SDS had advantages in laminate structure, which led to favorable applied properties of OBM. Results showed exchangeable cations in the interlayer of Mt had an impact on the activity of Mt, thus influenced basal spacing, content of anionic surfactants in the interlayer, thermal stability, surface polarity and the applied properties of CA-OMt in OBM. In the same modification process, Mt with more active cation in the interlayer can be modified more efficiently and have better applied properties. For further organic modification, adsorption study and industrial application of OMT, exchangeable cations in the interlayer of Mt should be regarded as a critical factor.

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